

Exciplex Formation upon Recombination of Radiation-Generated Radical Ion Pairs in Nonpolar Solutions

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Luminescence methods are among the most sensitive experimental physicochemical methods of investigation. They are also widely used for studying radiation-generated spin-correlated radical ion pairs in nonpolar solutions [1]. It is believed that recombination of a radical ion pair leads to formation of an excited luminophor molecule, which emits the detected quantum of luminescence. However, upon recombination, another molecule corresponding to the second partner of the pair is always located near the generated excited molecule. This can be a molecule of the same substance or a molecule of a second component specially introduced into a solution. As a result, not only the expected emission of a quantum of luminescence by the excited molecule but also the formation of excited complexes, such as exciplexes and excimers, can be observed. In addition, exciplexes under given conditions can also form in usual bulk diffusion-controlled reactions of the excited molecule with its partner; therefore, competition of two channels depending on the component concentrations in solution becomes possible.

Exciplexes are usually generated optically and studied in polar solutions [2, 3] by pulse methods. Exciplexes have also been studied in nonpolar solvents, including alkanes [4, 5]. All the systems studied in which exciplex formation is possible are analogous to the typical systems used in the radiation spin chemistry experiments, such as pyrene–*N,N*-dimethylaniline (DMA) in *n*-hexane [6] and anthracene–DMA in *n*-hexane [7]. The difference is only that, in the radiation spin chemistry experiments, X-ray irradiation of a sample is used, and the excited state is generated upon recombination of a radical ion pair formed when, for example, an electron is captured by an

anthracene molecule and the radical cation of the solvent (“hole”) is captured by a DMA molecule. X-ray radiation has been used in [8, 9], where it has been shown that pyrene excimer formation can occur through recombination of the $\text{Py}^{\bullet+}/\text{Py}^{\bullet-}$ radical ion pair.

Concentration-dependent (because of the competition of the pair recombination processes and the bulk reaction of the excited molecules with its partner) exciplex formation with red-shifted luminescence can considerably change the luminescence intensity distribution of the system as compared with the distribution of systems in which exciplexes are not formed. Therefore, it is of importance to study the luminescence spectra of such systems using X-ray excitation of a sample and compare the results with the data of experiments carried out with the use of optical excitation under the same experimental conditions.

In this work, we studied photo- and radiation-induced luminescence spectra of solutions of some donor–acceptor systems widely used in the radiation spin chemistry experiments, in particular, anthracene–DMA, *p*-terphenyl–DMA, and similar systems. In all the systems, one component was the same (DMA, a positive charge acceptor), and luminophors (electron acceptors) with either a rather long (~10–100 ns) or a short (~1 ns) excited state lifetime were selected as the second component. Exciplex formation in the systems with a luminescence lifetime of ~10–100 ns under optical excitation has been described in the literature [10]. Exciplexes for the *p*-terphenyl–DMA pair with an excited state lifetime of 1 ns have not been observed so far.

The luminescence spectra were recorded on a homemade setup [11]. The setup allows one to record luminescence spectra using X-ray and optical excitations under identical conditions. A BSV-27 X-ray tube was used for X-ray excitation, and a DRSh-500 high-pressure mercury lamp with a DMR-4 monochromator to select required spectral lines was used for optical excitation.

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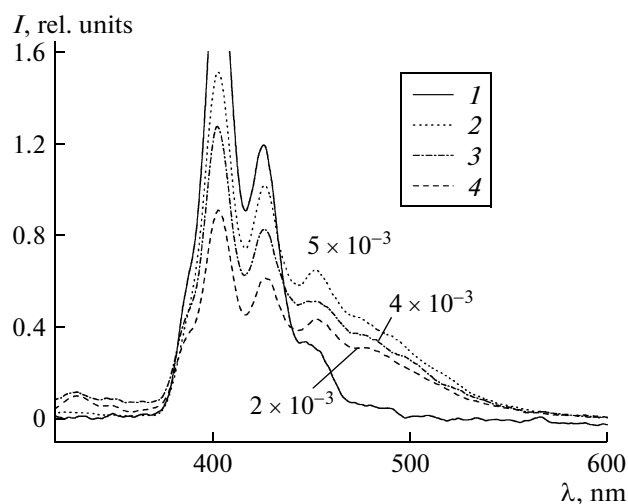


Fig. 1. X-ray-induced luminescence spectra of the anthracene–DMA system in *n*-dodecane: (1) 5×10^{-3} M anthracene; (2) 5×10^{-3} M anthracene, 10^{-2} M DMA; (3) 4×10^{-3} M anthracene, 10^{-2} M DMA; (4) 2×10^{-3} M anthracene, 10^{-2} M DMA.

The spectra were recorded in a molybdenum glass tube (which exhibits almost no intrinsic emission under X-irradiation) placed in a lead jacket with two slits: for incident X-rays or light and for outgoing light. When short-wavelength optical excitation (290 nm) was required, an identical quartz tube was used. The samples were degassed by three freeze–pump–thaw cycles. The experimental details and the choice of the tube material have been reported in [11].

In all experiments, additionally purified *n*-dodecane was used as a solvent. DMA was distilled over zinc powder before use; the fraction 193–195°C was used. The DMA purity was monitored by chromatography/mass spectrometry, which showed the presence of insignificant impurities (less than 1%) of *N*-methyl-aniline and *N,N*-dimethyl-*m*-aminoaniline. Anthracene and *p*-terphenyl (Aldrich) were used as received.

Figure 1 shows examples of X-ray-induced luminescence spectra for solution of anthracene and anthracene–DMA mixtures in *n*-dodecane. After the introduction of DMA into a solution, the spectrum shows, in addition to the intrinsic luminescence band of DMA (the weak line at 340 nm), a new long-wavelength band at about 500 nm. Analogous spectral patterns with the band at 500 nm (not shown in the figure) are also observed under optical excitation at 366 nm, in the absorption band of anthracene. According to [10], the new long-wavelength band is due to an exciplex. In this case, the anthracene excited state lifetime (5.6 ns) [12] turns out to be sufficient for the exciplex to form in the bulk reaction at a DMA concentration of 5×10^{-2} – 10^{-3} M.

With an increase in the concentration of one of the mixture components, its band and the exciplex band build up in the luminescence spectra under both X-ray

and optical excitation. To compare the efficiency of exciplex formation under X-ray and optical excitation, series of experimental spectra with varied anthracene concentration were processed in the following way. For the experiments with high anthracene concentrations ($\sim 10^{-3}$ M), the spectra of a mixture were decomposed into the spectra of separate components (anthracene, DMA, and exciplex) represented by Gaussian functions with the use of the global fitting procedure in Wolfram Mathematica software. An example of the spectrum decomposed into separate components is shown in Fig. 2.

Then, plots of I_{exc} versus I_{anth} were constructed, where the relative luminescence intensities of anthracene (I_{anth}) and exciplex (I_{exc}) were measured in the maxima of the bands obtained by spectrum decomposition, at 400 nm for anthracene and 480 nm for the exciplex. In these coordinates, each spectrum, i.e., each mixture composition, corresponds to one point. For analysis of the spectra of solutions with low anthracene concentrations ($\sim 10^{-4}$ M, optical density lower than 0.1) with a lower signal/noise ratio, the experimental spectra were preliminarily subjected to noise filtering with the use of standard Wavelet filtration or DIDP filtration procedures in Wolfram Mathematica software [13].

Figure 3 shows the plots of I_{exc} versus I_{anth} for optical and X-ray excitations. These plots are linear, and the slope of the straight lines for X-ray excitation is larger than that for optical excitation. In other words, for the same number of excited molecules, the number of exciplexes formed under X-ray excitation is always roughly twice as large as the number of exciplexes formed under optical excitation, which points to the appearance of an extra channel of exciplex formation through pair recombination. An analogous result was obtained using naphthalene as an electron acceptor ($\tau_f = 96$ ns).

In addition to the anthracene–DMA and naphthalene–DMA systems with the excited state lifetime $\tau_f = 5.6$ and 96.0 ns, respectively [12], we also studied the system with a shorter excited state lifetime, *p*-terphenyl–DMA. Exciplex formation in this system has not been observed so far, since *p*-terphenyl has a too short excited state lifetime (1 ns) for exciplex formation in the bulk reaction under optical excitation at reasonable quencher concentrations.

We found that, under X-ray excitation, the exciplex forms in the *p*-terphenyl–DMA system, which is manifested as a new band at 420 nm in the luminescence spectra. Examples of such spectra at varied *p*-terphenyl concentration are shown in Fig. 4. As shown, under optical excitation at 290 nm (spectra 5 and 6), depending on the concentrations of the mixture components, the luminescence spectrum was dominated either by *p*-terphenyl or by DMA (optically dense medium); no exciplex formation was observed. This demonstrates that, in the *p*-terphenyl–DMA system, the exciplex is formed only through recombina-

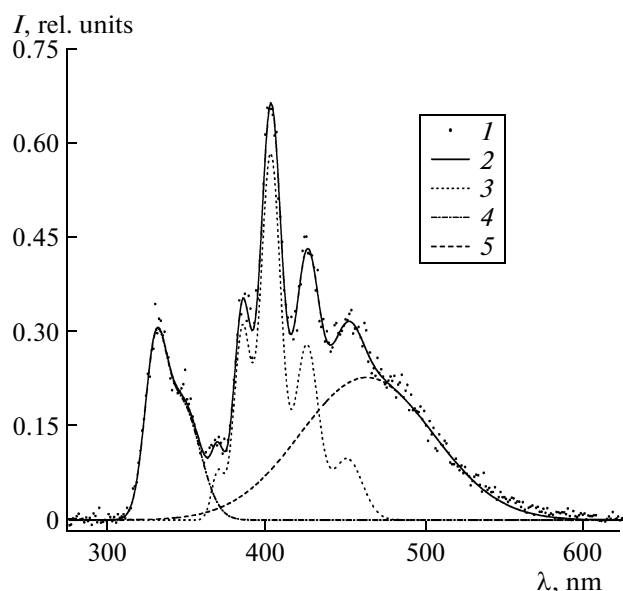
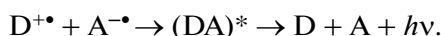
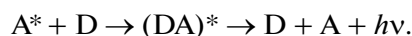


Fig. 2. Decomposition of the spectrum of a mixture (8×10^{-4} M anthracene, 10^{-2} M DMA) into the spectra of the components: (1) experimental data; (2–5) the luminescence spectra obtained after decomposition of spectrum for (2) the mixture, (3) anthracene, (4) DMA, and (5) exciplex.

tion, which is independent of the excited state lifetime:



Under optical excitation, the exciplex forms in the reaction of the excited acceptor molecule with the donor molecule captured from the bulk, which requires a sufficiently long excited state lifetime of the acceptor:



For *p*-terphenyl $\tau_f = 1$ ns so that the exciplex formation rate in the bulk reaction is small.

Thus, it has been shown that, for donor–acceptor systems, such as anthracene–DMA, recombination of radiation-generated geminate radical ion pairs in nonpolar solvents leads to exciplex formation. This essentially changes the luminescent properties of the samples and enables the competition between the recombination and bulk channels of exciplex formation. With a decrease in the excited state lifetime of the acceptor, exciplexes are not formed under optical excitation; under X-ray excitation, exciplexes can be formed directly at the stage of recombination, which make it possible to study exciplex formation for phosphors with extremely short excited state lifetimes.

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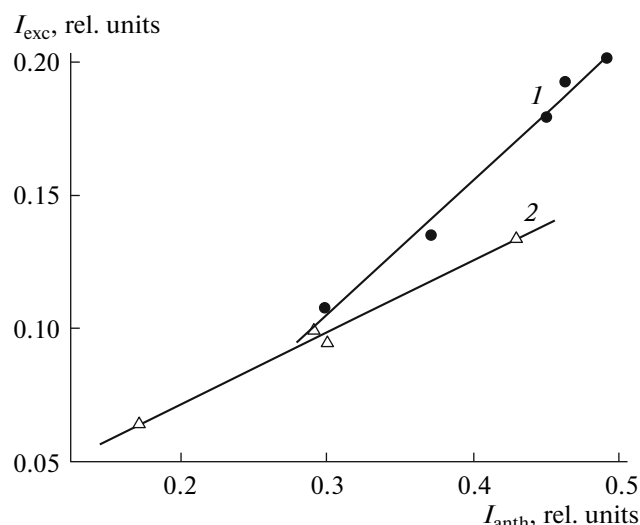


Fig. 3. Anthracene luminescence intensity vs. exciplex luminescence intensity: (1) X-ray excitation, $y = -0.04 + 0.51x$; (2) optical excitation at 366 nm, $y = 0.02 + 0.27x$.

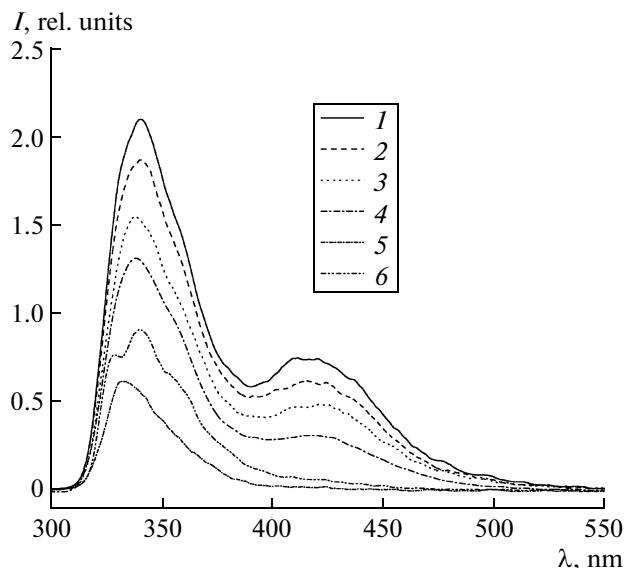


Fig. 4. Luminescence spectra of the *p*-terphenyl–DMA system in *n*-dodecane under (1–4) X-ray and (5, 6) optical excitation. X-ray excitation: (1) 8×10^{-4} M *p*-terphenyl, 10^{-2} M DMA; (2) 6.4×10^{-4} M *p*-terphenyl, 10^{-2} M DMA; (3) 4.8×10^{-4} M *p*-terphenyl, 10^{-2} M DMA; (4) 3.2×10^{-4} M *p*-terphenyl, 10^{-2} M DMA. Optical excitation: (5) 4×10^{-4} M *p*-terphenyl, 3×10^{-3} M DMA; (6) 8×10^{-5} M *p*-terphenyl, 9×10^{-3} M DMA.

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