

Highly efficient exciplex formation *via* radical ion pair recombination in X-irradiated alkane solutions for luminophores with short fluorescence lifetimes†

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Anatoly R. Melnikov,^{a,b} Evgeny V. Kalneus,^a Valeri V. Korolev,^a Igor G. Dranov,^a Alexander I. Kruppa^a and Dmitri V. Stass^{*a,b}

X-irradiation of alkane solutions of *N,N*-dimethylaniline with various organic luminophores produces characteristic emission bands ascribed to the corresponding exciplexes. In contrast to optical generation, which requires diffusion-controlled quenching of excited states, an additional channel of exciplex formation *via* irreversible recombination of radical ion pairs is operative here, which produces exciplexes in solution with high efficiency even for *p*-terphenyl and diphenylacetylene having fluorescence decay times of 0.95 ns and 8 ps, respectively. The exciplex emission band is sensitive to an external magnetic field and exerts a very large observed magnetic field effect of up to 20%, the maximum possible value under the conditions of the described experiment.

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Introduction

Techniques based on luminescence offer an exceptionally high sensitivity and are widely used in various fields of physical chemistry and biology. A possibility of introducing a fluorescent label into the process under study, or generation of a fluorescence state in the process, allows working *in situ* with very low concentrations of active species, down to single molecules. The excited state can be generated in a chemical or biological process (chemi- or bioluminescence), or can be directly excited by external light (photoluminescence). A separate class comprises the processes of the recombination luminescence, in which the electronically excited state is generated upon recombination of a radical ion pair. In particular, the recombination luminescence is commonly used to study radiation-generated spin-correlated radical ion pairs in non-polar solutions.¹ Here the radical ion pairs are generated, *e.g.*, by X-irradiation of an alkane solution, while their recombination results in formation of an excited molecule of the luminophore that emits the detected quantum of luminescence.

X-ray generation of electronically excited molecules *via* the step of radical ion pair recombination offers unique advantages of having the possibility of working with an optically dense sample (typical concentrations of positive charge acceptors used to obtain the radical cation of the pair are about 10^{-2} M or higher) while having an almost homogeneous formation of the excited molecules over the sample, as X-radiation is only weakly absorbed by an organic sample. Thus, emission from solutions of aromatic electron acceptors in pure *N,N*-dimethylaniline (DMA) was studied in pulse radiolysis experiments.²

Furthermore, under the conditions of X-ray generation, another molecule corresponding to the second partner of the pair is always found next to the excited molecule formed upon recombination. This can be either a molecule of the same compound, or a molecule of a different second component deliberately introduced into the solution. As a result, not only the expected emission of the quantum of luminescence by the excited molecule, but also the formation of excited complexes, such as exciplexes, becomes possible.³ The exciplexes under X-ray irradiation can also be formed *via* bulk diffusion-controlled reaction of the excited molecule with its partner common for optical generation, and thus a concentration-dependent competition between these two channels becomes possible. In addition, in the case of X-irradiation a further efficient channel for forming an excited solvent molecule by a very fast recombination of the primary radical ion pair “electron/solvent hole” is operative. The following excitation transfer to the molecule of the luminophore can lead to a more efficient formation of excited luminophore molecules

^aInstitute of Chemical Kinetics and Combustion SB RAS, 3, Institutskaya Str., 630090 Novosibirsk, Russian Federation. E-mail: stass@ns.kinetics.nsc.ru; Fax: +7 383 330 7350; Tel: +7 383 333 1561

^bNovosibirsk State University, 2, Pirogova Str., 630090 Novosibirsk, Russian Federation

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and, as a consequence, formation of exciplexes, under X-irradiation as compared to direct optical excitation of the luminophore. Finally, X-ray generation opens the way to form exciplexes for systems with a very short fluorescence lifetime of the luminophore molecule, as recombination creates optimal conditions for the exciplexes to form with high efficiency (the excited molecule and its partner are in close vicinity to each other) and without the need for time-consuming diffusional search for the partner.

Exciplexes are commonly generated by optical means and, although excimers and exciplexes were first observed in non-polar media (pyrene excimers⁴ and perylene/dimethylaniline exciplexes in benzene,⁵ respectively), in the context of the recombination luminescence they are studied mostly in more polar solutions, *e.g.* tetrahydrofuran, acetonitrile, or alcohols.⁶ Electrogenenerated chemiluminescence (ECL) is another method for generating a variety of electronically excited states which cannot be populated photochemically. The ECL generation from excited triplets,^{7,8} as well as excited state complexes such as excimers and exciplexes,^{9–11} is a typical example of emission from states that are not directly accessible for optical excitation. The differences between photo- and electro-generation of the excited states are due to the radical ion encounter complex that is the precursor for formation of the excited states in ECL. Bulk (as opposed to geminate) recombination of injected radical ions takes the place of the diffusion-controlled quenching of a local excited state, and ECL removes the requirement for sufficient lifetime of the excited state but requires sufficient stability of at least one of the radical ions of the pair. Radical ion recombination chemiluminescence can also be generated chemically, *e.g.*, by preparing radical anions *via* reduction with alkali metals and using Wurster's blue radical cation.^{12–15}

Several papers have reported studies of exciplexes in alkane liquids, including donor–acceptor pairs in alkanes^{16,17} similar to typical systems used in radiation spin chemistry, such as pyrene/DMA in *n*-hexane¹⁸ and in other alkanes,¹⁹ and anthracene/DMA in alkanes.²⁰ In this case the concentration-dependent formation of exciplexes with red-shifted emission bands and difficult to measure quantum yields of emission can significantly alter the luminescence properties of the system and thus the detected signal, especially if spectral limiting is used to improve the signal/noise ratio. This can be especially important when luminescence is used as a reporter to study other processes such as radical ion pair recombination, and warrants investigation of the spectra of luminescence from such systems under X-irradiation and their comparison with results of experiments under the same experimental conditions, but under optical excitation.

This work reports the spectra of photo- and radiation-generated luminescence from several donor–acceptor systems typical for radiation spin chemistry,¹ alkane solutions of naphthalene/DMA, *p*-terphenyl/DMA, and diphenylacetylene/DMA. One component of the system (DMA, positive charge acceptor) was held constant, as the other component (electron acceptor and luminophore) were chosen molecules with widely

varying lifetimes of the electronically excited state responsible for emission, τ_f , from about 100 ns to about 1 ns and to about 10 ps. Exciplexes in the studied systems for molecules with a τ_f of about 100 ns, accessible *via* optical excitation, are well-known and described in the literature.²¹ On the other hand, ionizing irradiation of alkane solution has rarely been used to study exciplex formation,² with most systems already known from optical excitation covered, such as excimers of pyrene in non-polar solutions,^{22,23} or polymeric systems, such as intramolecular exciplexes in polystyrene dissolved in cyclohexane²⁴ or exciplexes of the phenyl moiety and aliphatic amine in bulk epoxy resin.²⁵

Formation of excited states and exciplexes *via* the channel of radical ion pair recombination has another very important peculiarity. The multiplicity of the electronically excited state that forms upon recombination, singlet or triplet, corresponds to the collective electronic spin state of the recombining pair, which can be changed by application of external magnetic fields.¹ In a magnetic field of several mT the average singlet state population of a recombining pair originally formed in the singlet state, which is the case for radiation-generated pairs monitored by their recombination luminescence, is higher than the population in zero field due to less spin states available for singlet–triplet mixing. Since in solutions of organic luminophores, luminescence and exciplex formation are normally possible only from the singlet excited state, the yields of luminescence and exciplex formation *via* the channel of pair recombination become magnetosensitive. This forms the basis of the experimental methods of radiation spin chemistry, in which the dependence of the intensity of recombination luminescence from irradiated solutions on the external magnetic field is studied.^{26,27} On the one hand, this allows separation of the bulk and recombination channels of exciplex formation by studying their sensitivity to the magnetic field – the so-called magnetic field effect (MFE). On the other hand, when detecting in the emission band of the exciplex, this in principle allows an enhancement in the fraction of magnetosensitive emission, *i.e.*, the magnitude of MFE, especially for luminophores with short τ_f , when practically the entire intensity of this band is generated *via* the recombination channel due to the impossibility of forming the exciplex *via* bulk reaction.

MFE in the emission band of exciplexes upon optical generation is well-known²⁸ and is based on the reversibility of transitions between the radical ion pair state and the exciplex in the solvent of the corresponding viscosity and polarity.^{29–37} For systems lending themselves to exciplex formation, under ionizing irradiation MFE has so far only been observed in polar solvents, *e.g.* for the system pyrene/*N,N*-diethylaniline in methanol.³⁸ The magnetosensitivity of the exciplex emission band for systems with short τ_f (*p*-terphenyl, 0.95 ns, *etc.*) has not yet been reported. In this work we also studied the sensitivity of the obtained emission spectra to the external static magnetic field, and obtained the close to maximally possible MFE under these experimental conditions in the exciplex emission band for the system diphenylacetylene/DMA in *n*-dodecane.

Before passing on to results let us stress again that exciplexes produced by direct optical excitation of molecules, and MFE on their emission, have both been studied very extensively. General requirements and classic systems for their generation are known, and when exciplex formation should be avoided this can be done, *e.g.* by decreasing the concentration. In contrast to this, exciplex formation *via* the channel of recombination of radiation-induced radical ion pairs in alkanes, if possible at all in a given system, is a not widely discussed and, more importantly, principally unavoidable phenomenon. In addition, the magnetosensitivity of the exciplex emission band in this case is caused not by the presence of a finely tuned equilibrium between a radical ion pair and an exciplex generated from an electronically excited state, but rather by irreversible recombination of a radical ion pair to produce an electronically excited state.

Experimental

All spectra of recombination luminescence were obtained on a home-built Magnetically Affected Reaction Yield (MARY) spectrometer with X-ray excitation (CW X-ray tube BSV-27-Mo, Svetlana, St. Petersburg, Russia) and spectrally resolved detection (an MDR-206 grating monochromator, LOMO Photonics, St. Petersburg, Russia, objective focus length 180 mm, grating 1200 lines mm⁻¹, inverse linear dispersion 4.3 nm mm⁻¹, and a FEU-100 PMT) described elsewhere.³⁹ The spectrometer allows recording the spectra of recombination luminescence under low-level CW X-irradiation directly from samples studied in a radiation spin chemistry experiment, recording under these conditions the spectra of luminescence in an applied static magnetic field, and recording MFE resolved by wavelengths. The X-ray tube can also be changed for an optical source, currently a high pressure mercury lamp DRSh-500 with a double monochromator DMR-4 is used to select spectral line for excitation. This allows comparison of the spectra of CW photo- and radiation-induced luminescence from the same sample under the same experimental conditions.

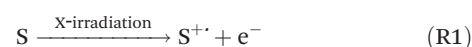
Experimental spectra were recorded in the following settings: X-ray tube 40 kV × 20 mA, estimated absorbed dose rate 85 krad h⁻¹; input/output slits of the monochromator in the detection channel 2.2 mm/2.2 mm (spectral resolution about 10 nm). For optical excitation: slits of the detection monochromator 0.7 mm/0.7 mm, excitation wavelength 366 nm or 290 nm, depending on the system under study, excitation light flux <10¹⁵ quanta s⁻¹. The samples were degassed by several freeze/pump/thaw cycles. All spectra were recorded in round ampoules with OD 5 mm made of molybdenum glass that was found to produce the lowest intrinsic luminescence under X-irradiation, or quartz, when a short-wave optical excitation was needed. To further suppress the background luminescence under X-irradiation the ampoule was placed in a lead jacket. The presented spectra were averaged over four 256 point wavelength scans and smoothed by sliding 5-point averaging. Intensities are given as arbitrary units corresponding to the output

signal of the detector, and are consistent for all spectra. A more detailed description of experimental parameters and the choice of material for the ampoule can be found in the earlier paper.³⁹

All samples were prepared using purified *n*-dodecane as the solvent. *N,N*-dimethylaniline (Aldrich, 99%) was freshly distilled over zinc powder, the 193–195 °C fraction was used. The purity of DMA was checked by chromatography-mass spectrometry; the only traceable impurities (<1%) were *N,N*-dimethyl-*m*-aminoaniline and *N*-methylaniline. Naphthalene, *p*-terphenyl (Aldrich, 99%), and diphenylacetylene (Aldrich, 98%) were used as received.

Reaction scheme

The basic scheme of processes occurring under low-level X-ray irradiation of alkane solutions of positive charge acceptors (electron donors, D) and electron acceptors (A) includes several stages¹ and is briefly outlined below. First the ionization of a solvent molecule (S) occurs yielding an electron and a solvent radical cation (solvent hole, S⁺):



The primary radical ion pair (S⁺/e⁻) is created so fast that the total spin state of the system does not change during the transition of the molecule into the radical ion pair. Since the ground state in most molecules is a singlet, the primary radical ion pair of solvent holes and electrons is formed in the spin-correlated singlet spin state.

The electron-hole distance in the pair is distributed with a characteristic length of about 6–10 nm, Coulombic attraction dominates over random thermal motion, and the pairs quickly, in the sub-nanosecond time domain, recombine to produce electronically excited solvent molecules:



The energy released upon recombination (R2) is almost always sufficient to produce both singlet and triplet S*, and the multiplicity of S*, singlet or triplet, coincides with the multiplicity of the recombining pairs.

After producing S* an excited positive charge acceptor (D*) or an excited electron acceptor (A*) can be formed *via* radiationless energy transfer:



Although the electron does recombine with a radical cation, it does not always recombine with its sibling radical cation. The ionizations occur inhomogeneously in space and form spurs containing several pairs. Within the spurs the average distance between the pairs is smaller than the characteristic pair size, the pairs overlap and cannot be treated as isolated, and cross-recombination of partners from different geminate pairs is possible.^{40,41} The experimentally determined fraction

of spin-correlated pairs for 40 keV X-ray irradiation is about 20% depending on the alkane⁴² and is less than 100% due to this cross-recombination in spurs. The cross-recombining pairs produce the statistical 1:3 ratio of singlet and triplet excited molecules.

The partners of the last surviving pair of the spur have some probability of being captured by a positive charge acceptor (electron donor, D) to form the donor radical cation $D^{+\cdot}$ and an electron acceptor (A) to yield the acceptor radical anion $A^{-\cdot}$:



Reaction (R6) proceeds if the electron affinity of molecule A is higher (less negative) than the energy of free electrons in the alkane with due account for solvation. This condition is nearly always met, *e.g.*, for aromatic molecules other than benzene and its methylated homologues. Reaction (R5) occurs if the ionization potential (IP) of molecule D is lower than IP of the solvent molecule. This is practically always true for alkane solutions of aromatic compounds or *N,S*-heteroatomic molecules. Both reactions in the overwhelming majority of cases are diffusion-controlled, but the mobility of electrons is about two orders of magnitude higher than the mobility of molecular ions, and therefore reaction (R6) for a given concentration of acceptors is much faster and can compete with primary pair recombination (R2) for concentrations of A about 10^{-5} – 10^{-4} M. Electron capture (R6) extends the typical lifetimes of the pair from sub-nanosecond up to about 10 ns, and donor radical cation $D^{+\cdot}$ formation *via* reaction (R5) can then become appreciable for concentrations of D about 10^{-3} – 10^{-2} M. The spin correlation in the pair is not disturbed by charge transfer to acceptors, and if the scavenged primary pair ($S^{+\cdot}/e^{-}$) belonged to those 20% of spin-correlated pairs mentioned above, the secondary radical ion pair ($D^{+\cdot}/A^{-\cdot}$) is also formed in a spin-correlated state.

Similar to reaction (R2), recombination of the secondary radical ion pairs, *i.e.*, back electron transfer from $A^{-\cdot}$ to $D^{+\cdot}$, in nonpolar solution proceeds with nearly 100% efficiency at the first encounter of the mutually attracted radical ions, and releases energy sufficient for electronic excitation of one of the pair molecules (A^* or D^*) in any multiplicity:



The formed A^* or D^* can emit the detected quantum of luminescence, but in solution normally only fluorescence can be observed, and thus the intensity of the recombination luminescence reflects the amount of singlet state recombinations.

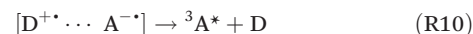
Recombination conserves the collective spin state of the system, and the multiplicity of the forming product coincides with the multiplicity of the pair at the moment of recombination. For random pairs this would give the statistical factor of $\frac{1}{4}$ for singlet recombinations. However, for spin-correlated pairs

the fraction of singlet radical ion pairs may vary, *e.g.*, it starts from 1 when the pair is created in reaction (R1). The secondary pairs ($S^{+\cdot}/A^{-\cdot}$) and ($D^{+\cdot}/A^{-\cdot}$) inherit the spatial distribution of the primary pairs they are formed from, but lack highly mobile electrons, and thus have typical lifetimes of the order of 10 ns, which are sufficient to alter their electronic spin multiplicity by magnetic interactions of electron spins of the radical ions with magnetic nuclei like protons and with an external magnetic field, if the latter is applied.^{43,44} Thus the sequence of reactions leading to recombination luminescence (R7, R8) is magnetosensitive.

Similar processes of recombination luminescence are also known to occur in the electrogenerated chemiluminescence (ECL).^{7–11} Suitable electron acceptor and electron donor molecules A and D are reduced and oxidized in one-electron processes on the respective electrodes. The injected oppositely charged radical ions form an encounter complex that is the precursor for formation of the excited states:



The complex is normally lower in energy than any local singlet excited state and can undergo electron transfer yielding an excited triplet molecule (R10), produce an exciplex in equilibrium with the complex (R11), or simply decompose by a radiationless pathway (R12):



The concentration of triplets can be high enough as rather large charge densities can be injected electrochemically. This leads to triplet–triplet annihilation resulting in excited singlet molecules:



An ECL system can also be directly excited by optical means to produce, *e.g.*, A^* , which can either deactivate locally, or again form the exciplex if it meets its partner while in the excited state in a process that is common for photogeneration of exciplexes:



The emission intensity of exciplexes relative to the singlet state generated by ECL is higher than for optical excitation for the same sample since in the case of ECL all excited states are generated from one precursor, the encounter complex $[D^{+\cdot} \cdots A^{-\cdot}]$,⁹ while under photoexcitation an excited molecule of A can emit without ever encountering its partner D molecule. ECL also removes the requirement for sufficiently long lifetime of the excited state implied by reaction (R14), and exciplexes can be generated electrochemically from molecules with very rapid deactivation, like *p*-terphenyl¹¹ or benzophenone.⁹

On the other hand, in ECL the electrochemically generated radical ions need to be taken into solution, and have to diffuse

substantial distances even when using microelectrodes, and thus require supporting electrolytes and relatively higher permittivity to stabilize them. The solvents are rarely less polar than dimethoxyethane or tetrahydrofuran ($\epsilon \sim 7.5$), and even then the choice of radical ions is limited, *e.g.*, *N,N*-dimethylaniline has to be changed to 4,*N,N*-trimethylaniline to sufficiently stabilize its radical cation.

In this work we would like to draw attention to the observation that the recombination luminescence in X-irradiated alkane solutions can also provide an efficient way to generate exciplexes from molecules with arbitrary short-lived excited states and, furthermore, radical ions with lifetimes of just 10 ns *via* an irreversible process similar to reactions (R9, R11):



A similar reaction was earlier discussed for excimers of pyrene ($\tau_f = 370$ ns in degassed cyclohexane)⁴⁵ in irradiated alkanes.^{22,23} Exciplex formation in reaction (R14) *via* bulk quenching of electronically excited molecules produced in reactions (R3, R4, R7, R8) is also possible, but requires sufficient τ_f .

The complete scheme of radiation chemical processes can in general be much more complex than that outlined in this section,^{46–49} but the discussed key reactions are sufficient to describe the situation of relatively low-level CW X-ray excitation as employed in this work.¹ For the used absorbed dose rate of 85 krad h⁻¹ the estimated steady-state concentrations of radical ion pairs in the sample are of the order of 100 homogeneously distributed pairs per sample of 1 mL, as also measured directly under similar conditions for isoctane under 30 keV X-ray irradiation.⁵⁰ This number is determined by the balance of generation and recombination, and is in part so low because of the short pair recombination time. While the concentration of other more longer-lived species like excited triplets can reach up to 10⁷ per sample, this is still just $\sim 10^{-14}$ M, so all processes that are higher than first order with respect to active species, like triplet–triplet annihilation, can be omitted. The matching optical excitation used in this work was also low-level with the estimated flux of quanta less than 10¹⁵ s⁻¹. Thus the formation of singlet excited states of donors or acceptors *via* triplet–triplet annihilation can be neglected under our experimental conditions.

Results and discussion

Radiation generation of exciplexes

Fig. 1 shows typical spectra of the radiation-generated luminescence for solution of naphthalene and mixtures of naphthalene and DMA in *n*-dodecane. When DMA is introduced into the solution, not only its intrinsic emission band (that nearly coincides with the emission band of naphthalene) appears in the spectrum, but also a new red-shifted band in the region of 400 nm appears belonging to the exciplex.³⁹ Fig. 2 shows that similar spectra, bearing the exciplex emission band, also appear upon optical excitation at 290 nm, in the absorption

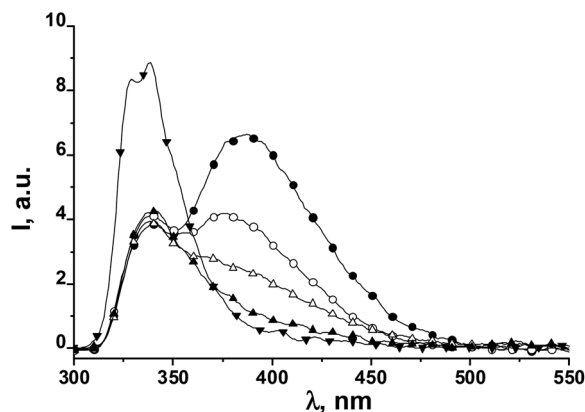


Fig. 1 Spectra of the radiation-generated luminescence for solutions of naphthalene and DMA in *n*-dodecane. DMA concentration is 10⁻² M for all spectra, naphthalene concentration: ● – 6.4 × 10⁻³ M, ○ – 3.2 × 10⁻³ M, △ – 1.3 × 10⁻³ M, ▲ – 1 × 10⁻³ M. For comparison the spectrum of the solution of only 5 × 10⁻³ M naphthalene is shown with ▼.

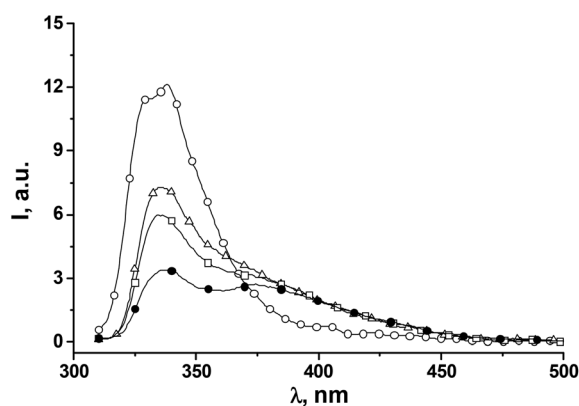


Fig. 2 Spectra of the luminescence for solutions of naphthalene and DMA in *n*-dodecane upon optical excitation at 290 nm. DMA concentration is 10⁻² M for all spectra, naphthalene concentration: △ – 2 × 10⁻³ M, □ – 4 × 10⁻³ M, ● – 5 × 10⁻³ M. For comparison the spectrum of the solution of only 5 × 10⁻³ M naphthalene is shown with ○.

band of naphthalene (light absorption by DMA does not lead to exciplex formation, *vide infra*). A similar red-shifted band was earlier observed and ascribed to the exciplex in the anthracene/DMA system.^{51,52} Fig. 3 shows a pair of selected spectra from one and the same sample under optical excitation and X-irradiation, normalized to the intensity of the intrinsic emission band. It can be seen that under X-irradiation the relative intensity of the exciplex emission band is significantly higher, similar to the ECL/optical comparison mentioned above.⁹

In the case of the naphthalene/DMA system the lifetime of the excited state of naphthalene (96 ns)⁵³ is sufficient to form an exciplex *via* the conventional bulk diffusion-controlled reaction at a DMA concentration in the range 5 × 10⁻²–10⁻³ M. However, as compared to the anthracene/DMA system, in the case of the naphthalene/DMA system the complication of the optically dense medium arises. As naphthalene and DMA have much overlapping absorption spectra and similar extinction coefficients at 290 nm (molar extinction coefficients

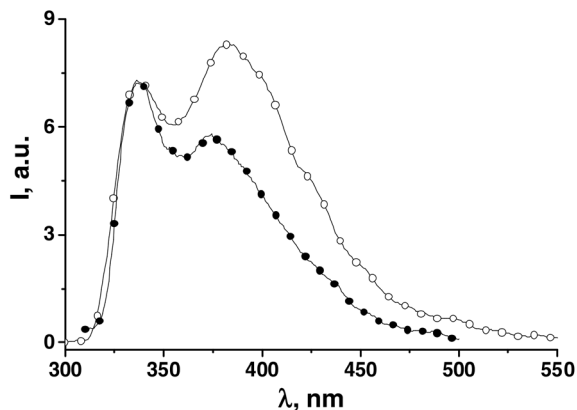


Fig. 3 Luminescence spectra for an *n*-dodecane solution of 5×10^{-3} M naphthalene and 10^{-2} M DMA upon optical excitation at 290 nm (●) and X-ray irradiation (○), other experimental conditions being the same. Spectra normalized at 340 nm.

of about 3200 and 2200 $\text{M}^{-1} \text{cm}^{-1}$, respectively),⁵³ neither naphthalene can be excited separately, nor low concentrations of naphthalene of the order of 10^{-4} M can be used, which were both possible for anthracene having rather prominent absorption at 366 nm. Thus, upon excitation of the mixture at 290 nm the exciting light is completely absorbed in the sample, mostly by DMA (concentration about 10^{-2} M, $\text{OD} \gg 1$).

As the concentration of one of the components in the mixture is increased, the intensities of both the intrinsic luminophore emission band (the emission bands of naphthalene and DMA practically coincide) and the exciplex emission band increase both under X-ray and optical excitation of the sample. To compare the efficiency of exciplex formation upon optical and radiation generation, a series of experimental spectra with varied concentrations of naphthalene was processed using a modified internal calibration procedure first suggested earlier⁵² for a simpler system anthracene/DMA. First the individual emission spectra of naphthalene and DMA (only one component in solution) were recorded under the same conditions and represented as sets of Gaussian functions with fixed positions, widths and relative amplitudes using the built-in fitting procedure *FindFit* in the Wolfram Mathematica 7.0 environment. The thus-obtained combinations, shown in Fig. 4, were then used as initial data for decomposition of the spectra of mixtures into the combinations of Gaussian functions representing the spectra of the three components (naphthalene, DMA, and exciplex). The results of such decomposition for a representative spectrum are also shown in Fig. 4. Then the ratios of the maximum intensity of the extracted exciplex emission band to the sum of maximum intensities of the extracted intrinsic luminophore bands were plotted vs. the concentration of naphthalene in the range of its concentrations 10^{-3} – 5×10^{-3} M for both optical and X-ray excitation. As discussed earlier,⁵² this provides the internal calibration of the amount of generated excited molecules, which is not straightforward to estimate under X-irradiation, and further deals with the ambiguity of extracting the intensities of

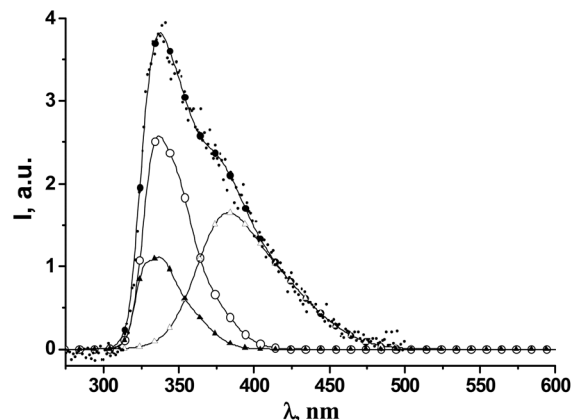


Fig. 4 Decomposition of the spectrum of the radiation-generated luminescence for the solution of 1.5×10^{-4} M naphthalene and 10^{-2} M DMA in *n*-dodecane into combinations of Gaussian functions representing the spectra of individual components (naphthalene, DMA, and exciplex). Smooth curves give the model spectra of the luminescence for: ○ – naphthalene, ▲ – DMA, △ – exciplex, ● – mixture, scattered dots show the experimental spectrum being decomposed.

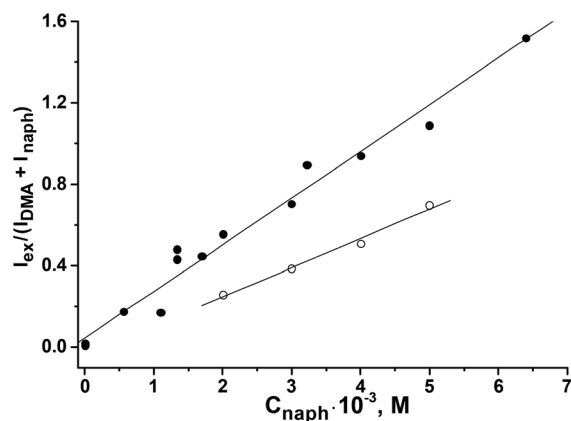


Fig. 5 Experimental dependences of the ratio of the intensity of the exciplex emission band (400 nm) to the sum of intensities of the intrinsic DMA and naphthalene emission bands (320 nm) on the concentration of naphthalene and their linear fits. The figure shows: ● – X-irradiation of the sample, $y = 0.02 + 0.23x$; ○ – optical excitation at 290 nm, $y = -0.01 + 0.14x$.

the overlapping intrinsic emission bands of the two compounds. The intensity of the exciplex emission band I_{exp} and the total intensity of intrinsic emission bands I_{tot} (DMA + naphthalene) were measured at 400 nm and at 350 nm, respectively.

The dependence of the ratio $I_{\text{exp}}/I_{\text{tot}}$ thus obtained on the concentration of naphthalene under optical excitation turns out to be practically linear (Fig. 5), which can be rationalized as follows. Measuring intensities in quanta per unit time, the intensity of intrinsic emission of naphthalene can be written as:

$$I_{\text{naph}} = I_{\text{naph}}^{\text{abs}} \frac{\varphi_{\text{naph}} \tau_{\text{f}}^{-1}}{k_{\text{d}} [\text{DMA}] + \tau_{\text{f}}^{-1}} \quad (1)$$

where $I_{\text{naph}}^{\text{abs}}$ is the number of light quanta absorbed by naphthalene, τ_f is the fluorescence decay time of naphthalene (96 ns), φ_{naph} is the emission quantum yield of naphthalene (0.23), and k_d is the diffusion-controlled rate constant in *n*-dodecane ($8.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).⁵⁴ The numerator gives the reciprocal of the natural lifetime. The corresponding expression for the intensity of intrinsic emission of DMA is given by

$$I_{\text{DMA}} = I_{\text{DMA}}^{\text{abs}} \cdot \varphi_{\text{DMA}} \quad (2)$$

where φ_{DMA} is the emission quantum yield of DMA (0.11).⁵³ In this case reaction between an excited DMA molecule and a ground-state naphthalene molecule can be neglected due to the shorter fluorescence lifetime of DMA molecules (2.4 ns)⁵³ and the lower concentration of naphthalene (see ESI†).

The yield of exciplexes formed from the excited naphthalene molecules can be determined by:

$$\varphi_{\text{exp}} = \frac{k_d[\text{DMA}]}{k_d[\text{DMA}] + \tau_f^{-1}} \quad (3)$$

Then the number of exciplexes formed from excited molecules of naphthalene will be equal to:

$$N_{\text{exp}} = I_{\text{naph}}^{\text{abs}} \cdot \varphi_{\text{exp}} \quad (4)$$

Finally, the intensity of exciplex emission is proportional to their number:

$$I_{\text{exp}} = N_{\text{exp}} \gamma_e = I_{\text{naph}}^{\text{abs}} \frac{k_d[\text{DMA}]}{k_d[\text{DMA}] + \tau_f^{-1}} \gamma_e \quad (5)$$

where the proportionality constant is the (unknown) fluorescence quantum yield of the exciplex.

As already mentioned, excitation at 290 nm produces both excited DMA and naphthalene molecules, and for rather high concentrations of compounds employed (about 10^{-3} M for naphthalene and 10^{-2} M for DMA) the system must be treated as optically dense. In this situation the fraction of light absorbed by naphthalene $I_{\text{naph}}^{\text{abs}}$ (and similarly by DMA) depends on the relative optical densities of naphthalene (D_{naph}) and DMA (D_{DMA}) and is given by the following expression:⁵⁵

$$I_{\text{naph}}^{\text{abs}} = \frac{D_{\text{naph}}}{D_{\text{naph}} + D_{\text{DMA}}} I_{\Sigma}^{\text{abs}} \quad (6)$$

Substituting the known values of parameters in expressions (eqn (1–6)) and plotting the ratio of I_{exp} to $I_{\text{naph}} + I_{\text{DMA}}$ vs. the concentration of naphthalene produces nearly linear graphs in the range of naphthalene concentrations 10^{-3} – $5 \times 10^{-3} \text{ M}$ (see ESI†). The experimental plot in these coordinates is shown in Fig. 5 together with its least-squares linear fit, each point on such a graph corresponds to a given mixture composition. Thus for optical excitation the increase of exciplex emission on the increase of naphthalene concentration is due to the increase of the fraction of light absorbed by naphthalene under conditions of (practically) total absorption of excitation light. This also demonstrates that light absorbed by naphthalene

is more efficiently converted to exciplex emission than light absorbed by DMA (see ESI†).

To compare the efficiencies of exciplex formation upon optical and X-ray generation the same processing and coordinates were also used to evaluate the radiation-generated emission spectra. The experimental results are also summarized in Fig. 5. The graph is also linear, with the slope for X-irradiation approximately by a factor of two exceeding the slope for optical excitation. In other words, it is experimentally obtained that for an equal number of quanta emitted from excited molecules the number of forming exciplexes under X-irradiation is always larger than that under optical excitation, revealing the additional channel of exciplex formation *via* the step of radical pair recombination. The underlying theoretical description in the case of X-irradiation is much more complex and must explicitly take into account the kinetics of geminate recombination of the radical ion pair, and is currently under development. A similar result was earlier obtained for a simpler system utilizing anthracene instead of naphthalene ($\tau_f = 5.6 \text{ ns}$).⁵²

In continuation of the series of systems with a τ_f of about 100 ns (naphthalene/DMA) and a τ_f of about 10 ns (anthracene/DMA), a system with still shorter τ_f of 0.95 ns,⁵³ *p*-terphenyl/DMA, was studied. Formation of exciplexes in this system has not been reported earlier, since τ_f of *p*-terphenyl is too short to form exciplexes in the bulk diffusion-controlled reaction upon optical excitation and at reasonable quencher (DMA) concentrations. Exciplexes from *p*-terphenyl and 3-*p*-tolylamine were generated electrochemically in tetrahydrofuran.¹¹ However, exciplexes do form in the solution of *p*-terphenyl and DMA in *n*-dodecane under X-irradiation, as revealed by a new red-shifted emission band in the region of 420 nm. Examples of such spectra of luminescence for varied concentrations of *p*-terphenyl are shown in Fig. 6. As the figure also demonstrates, upon optical excitation at 290 nm the

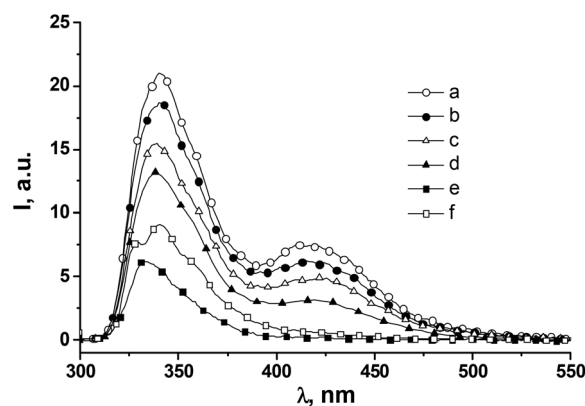


Fig. 6 Spectra of the luminescence for solutions of *p*-terphenyl and DMA in *n*-dodecane under X-irradiation and optical excitation at 290 nm. X-irradiation: a (○) – $8 \times 10^{-4} \text{ M}$ *p*-terphenyl, 10^{-2} M DMA; b (●) – $6.4 \times 10^{-4} \text{ M}$ *p*-terphenyl, 10^{-2} M DMA; c (△) – $4.8 \times 10^{-4} \text{ M}$ *p*-terphenyl, 10^{-2} M DMA; d (▲) – $3.2 \times 10^{-4} \text{ M}$ *p*-terphenyl, 10^{-2} M DMA; optical excitation: e (■) – $8 \times 10^{-5} \text{ M}$ *p*-terphenyl, $9 \times 10^{-3} \text{ M}$ DMA, f (□) – $4 \times 10^{-4} \text{ M}$ *p*-terphenyl, $3 \times 10^{-3} \text{ M}$ DMA.

emission spectrum of either predominantly *p*-terphenyl or predominantly DMA is observed, depending on the concentrations of components (again the case of optically dense medium with competing absorbers); quite expectedly, no signs of exciplexes were found in either case.

It is worth stressing that under X-irradiation exciplexes in this system form at very low concentrations of the components, down to 5×10^{-4} M of both *p*-terphenyl and DMA simultaneously. Fig. 7 shows the spectra of the luminescence from mixtures at low concentrations of the components, as well as emission spectra of only DMA and only *p*-terphenyl (only one component in solution). To highlight the formation of exciplexes all spectra were normalized to the maximum of the *p*-terphenyl emission band at 350 nm. A clear increase in emission intensity can be seen at 420 nm, in the emission band ascribed to the exciplex. As demonstrated by emission spectra under optical excitation discussed above, the bulk reaction of DMA with excited *p*-terphenyl molecules can be ruled out due to very short τ_f . However, in the case of X-irradiation the radical anion of *p*-terphenyl and the radical cation of DMA at the moment of recombination are close to each other, so that their parent molecules reformed upon back electron transfer are capable of forming the exciplex irrespective of the bulk concentrations of both *p*-terphenyl and DMA. The amounts of the formed radical ions of *p*-terphenyl and DMA depend on the respective bulk concentrations, but, once the radical ions have formed, the irreversible and almost 100% recombination of the radical ion pairs produces both electronically excited luminophore molecules and exciplexes.

Summing up the reaction channels, in the system *p*-terphenyl/DMA exciplexes are formed mostly *via* the channel of radical ion pair recombination (R15) that does not depend on the lifetime of the excited state τ_f . In the case of direct optical excitation exciplexes are formed *via* the channel of quenching of the excited acceptor molecule by a donor molecule found in

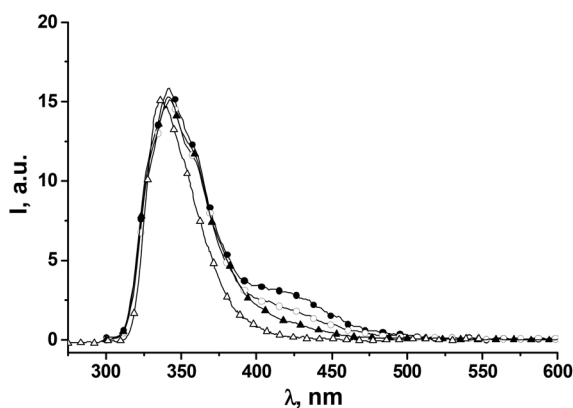


Fig. 7 Spectra of the radiation-generated luminescence for solutions of *p*-terphenyl and DMA in *n*-dodecane at low concentrations of components. All spectra normalized to the maximum of the *p*-terphenyl emission band at 350 nm. The concentrations of the components are: ● – 6×10^{-4} M *p*-terphenyl, 10^{-3} M DMA, ○ – 6×10^{-4} M *p*-terphenyl, 8×10^{-4} M DMA. For comparison also shown are spectra for solutions of only 10^{-2} M DMA (Δ) and only 0.95×10^{-3} M *p*-terphenyl (\blacktriangle).

the bulk (R14), which depends on the lifetime of the excited state τ_f . For *p*-terphenyl $\tau_f = 0.95$ ns, and the rate of exciplex formation *via* the channel of bulk reaction at the used concentration of DMA is vanishingly low.

Magneto-sensitivity of the exciplex emission band

Application of an external magnetic field to the sample produces observable changes in the recombination process by changing the relative amounts of singlet and triplet recombinations. Magnetic field effects, *i.e.*, the dependence of the reaction yield on the applied magnetic field in non-polar solutions of donor–acceptor systems arise only at the step of geminate recombination of the radical ion pair.^{1,43} Fig. 8 shows the spectra of luminescence under X-irradiation from the same sample of the *p*-terphenyl/DMA system, taken under the conditions described above in the magnetic field of 20 mT and without an applied field. As the figure demonstrates, the intensity of the exciplex emission band in the applied field is about 15% higher than without the applied field. No MFE was observed for optical excitation. MFE in this case is a clear indication of exciplex formation *via* the channel or radical pair ion recombination. A smaller, although discernible, effect is also observed on the overlapping emission bands of *p*-terphenyl and DMA. This may be caused by both extension of the broad exciplex emission band under the *p*-terphenyl/DMA emission band, and incomplete transformation into the exciplex of electronically excited *p*-terphenyl molecules formed upon recombination of the *p*-terphenyl^{•−}/DMA^{•+} pair. Earlier a similar MFE was also reported for the naphthalene/DMA system.³⁹

MFE was obtained for several other systems comprising DMA where exciplex formation was found to be possible, both with longer τ_f , including the already mentioned naphthalene ($\tau_f = 96$ ns) and biphenyl ($\tau_f = 16$ ns),⁵³ and in a system with even shorter τ_f , diphenylacetylene/DMA. Diphenylacetylene is a very interesting partner here, because it has a very low quantum yield of fluorescence (0.0036)⁵⁶ and thus produces virtually no intrinsic luminescence in solution, and the

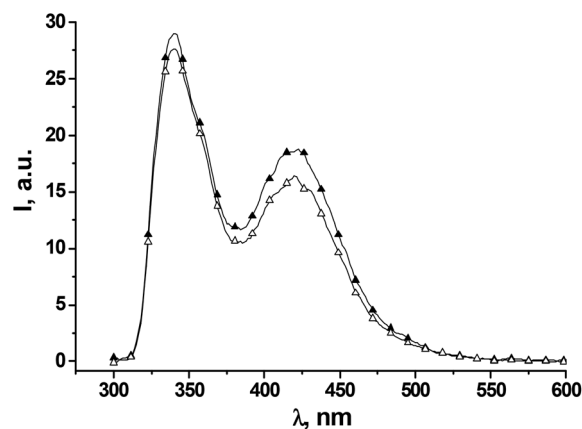


Fig. 8 Spectra of the radiation-generated luminescence for solutions of 0.95×10^{-3} M *p*-terphenyl and 10^{-2} M DMA in *n*-dodecane recorded in the applied magnetic field 20 mT (\blacktriangle) and without the field (Δ).

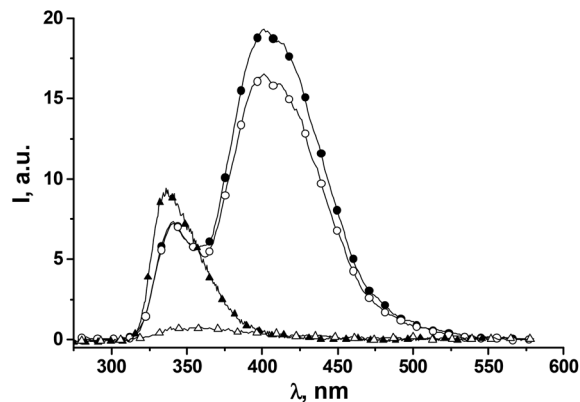


Fig. 9 Spectra of the radiation-generated luminescence for solutions of 2.5×10^{-2} M diphenylacetylene (Δ), 10^{-2} M DMA (\blacktriangle), and 2.5×10^{-2} M diphenylacetylene plus 10^{-2} M DMA in *n*-dodecane in the magnetic field 20 mT (\bullet) and without the field (\circ).

lifetime of the fluorescing state is very short, only 8 ps;^{54,57} therefore, as was checked, it does not form exciplexes with DMA upon optical excitation of non-polar solutions. Fig. 9 shows the spectra of luminescence under X-irradiation of solutions of only diphenylacetylene, only DMA, and the mixture of diphenylacetylene/DMA, in the latter case with or without an applied magnetic field of 20 mT. Upon addition of DMA the very weak emission band of diphenylacetylene is transformed into a prominent red-shifted exciplex emission band at 420 nm that shows MFE of 20%. The intrinsic DMA emission band at 340 nm shows no MFE, as excited DMA under these conditions is formed either by recombination of its radical cation with free electrons produced by ionization of the solvent molecule, or by energy transfer from electronically excited solvent molecules produced by recombination of solvent radical cations with free electrons. As is well known, both recombination processes proceed very fast due to the high mobility of electrons in alkanes and thus produce no MFE.¹

The magnitude of MFE obtained in the exciplex emission band for the diphenylacetylene/DMA system deserves special attention. This value is close to the experimentally found fraction of spin-correlated radical ion pairs under these conditions,^{42,58} and thus to the maximally attainable magnetic field effect. In theory, the maximum MFE for a spin-correlated radical ion pair is 100% (doubling of the emission signal in an applied magnetic field), corresponding to a switch from four spin states available for singlet–triplet mixing, S , T_0 , T_+ , T_- , in zero field to only two states, S , T_0 , in the applied field. However, as discussed in the section on the reaction scheme, upon ionization of the solvent molecules under X-irradiation the produced radical ion pairs are not isolated, but rather form spurs containing several overlapping pairs. The oppositely charged solvent radical cations and free electrons in the spur rapidly recombine with the first encountered partner, and the spin correlation is partially lost in such cross-recombinations. Finally, at most only a single pair is left for capture by acceptors to form the target radical ion pair $A^{\cdot-}/D^{\cdot+}$, and under

the conditions of the described experiment only about 20% of them remain correlated and thus can in principle contribute to MFE formation. The 15% MFE in the exciplex emission band for the *p*-terphenyl/DMA system described above is also very large for a radiation-generated pair, in which normal MFE on the commonly observed total intensity of the recombination luminescence rarely exceed 1%.¹

The presence of MFE in the exciplex emission band for systems with the fluorescence lifetime varying from 10 ps to 100 ns indicates that exciplexes are indeed formed *via* the channel of radical ion pair recombination. In the systems *p*-terphenyl/DMA and diphenylacetylene/DMA with very short τ_f this channel becomes the only possibility, and MFE in the exciplex emission band comes close to its maximally attainable values.

Conclusions

Summing up, it is shown for several typical donor–acceptor systems that recombination of radiation-generated radical ion pairs in alkanes can produce exciplexes. This can substantially change the luminescence properties of the sample, from creating an additional red-shifted emission band that borrows part of intensity from the expected intrinsic luminophore emission band to converting an essentially dark system to a luminescing exciplex, as was the case with diphenylacetylene. Furthermore, the luminescence properties of the sample become concentration-dependent due to the competition with bulk reaction of exciplex formation *via* diffusion-controlled quenching of the excited molecule. X-ray generation of exciplexes *via* the recombination channel opens the way to hitherto inaccessible exciplexes from luminophores with an arbitrary short fluorescence lifetime and unstable radical ions provided such exciplexes are energetically and sterically possible, which may be important for experimental validation of calculations predicting such complexes. Isolated exciplexes can be produced homogeneously in the bulk from nearly arbitrary donor–acceptor systems in solutions of an arbitrary optical density, up to pure dyes. Using radiolysis of nonpolar liquids like alkanes, the radical ions that are required for this can be produced from a vast variety of molecules. This also opens the possibility to tune donor–acceptor pairs for prospective bridged systems without actually synthesizing them, as the partners of radiation-generated radical ion pairs will find each other in non-polar solution with close to unit probability, and will generate an electronically excited state and, as was found, exciplexes, upon recombination. The exciplex emission band is also sensitive to the external magnetic field due to spin evolution of radical ion pairs that irreversibly recombine to generate electronic excitation. It is the fluorescence from the recombination products which is then spectrally shifted to a different emission band. This opens the way to enhance the observable MFE in radiation spin chemistry experiments, as detection of the exciplex emission band can help get rid of the background luminescence always generated upon high-energy irradiation. Finally, the radiation generation of the recombination

luminescence in solution is probably a closer mimic of the electroluminescence in doped polymeric systems than the electrochemiluminescence in solution or the photoluminescence, and can be used to tune the charge transport and light generation components of organic light-emitting systems like OLEDs,⁵⁹ as demonstrated recently for a prototypic Alq₃ system.⁶⁰

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