PAPER

Estimation of the fluorescence lifetime for optically inaccessible exciplexes in nonpolar solutions under ionizing irradiation

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X-irradiation of nonpolar solutions likely provides a possibility to create exciplexes for any donor–acceptor pair that would energetically and sterically allow this. Thorough study and characterization of X-radiation generated exciplexes usually cannot be carried out with conventional methods because of the complex and non-exponential formation and decay dynamics of these species. In this paper, we present a simple and universal experimental approach for the estimation of fluorescence lifetimes (τ_F) of X-radiation generated exciplexes. The suggested procedure is based on the comparison of quenching of the exciplex emission band and the emission band from a standard luminophore with a known excited state lifetime by dissolved oxygen. Using this approach we report the τ_F values for two systems with optically inaccessible exciplexes, diphenylacetylene–*N,N*-dimethylaniline (DMA) and *p*-terphenyl–DMA, and for two typical exciplex forming systems, naphthalene–DMA and anthracene–DMA. All the found τ_F values for the X-radiation generated exciplexes lie in the range of 50–70 ns. The accuracy of this approach was checked by time-resolved measurements under X- or near-UV irradiation for those pairs, whose properties make this feasible. The proposed method gives a possibility to avoid a complex numerical evaluation of the non-exponential kinetics of recombination luminescence, and can be used to estimate the characteristic τ_F values for luminophores and excited complexes formed under X-radiation.

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1.   Introduction

Ionizing irradiation of X-range provides a convenient means for the generation of electronically excited states in nonpolar solutions. A key step in this process is the recombination of the generated radical ion pair *via* electron transfer from a radical anion to a radical cation that releases sufficient energy to produce electronically excited states of the solute.[1,2] Radical ion pair recombination can also lead to the formation of excited state complexes (exciplexes) between the parent molecules of the radical ion pair, due to the close proximity of the excited molecule and its partner. In the case of X-radiation, exciplexes could be obtained for systems with an extremely short lifetime of the excited state of the employed electron

acceptor.[3] Therefore, under X-radiation exciplexes could be generated not only for selected special systems, such as pyrene–*N,N*-dimethylaniline (DMA), but also, in all likelihood, in practically any suitable donor–acceptor pair that would energetically and sterically allow this. On one hand, this provides nearly unlimited possibilities for the experimental generation of exciplexes, which was earlier discussed in our previous paper.[3] On the other hand, the geminate recombination of radical ion pairs results in complex and non-exponential kinetics of recombination luminescence that significantly complicates time-resolved studies. Commonly used optical techniques for exciplex lifetime characterization are not suitable for the X-radiation generated exciplexes, and new specifically adapted methods have to be developed. In this work we suggest a simple and universal experimental approach for estimation of the fluorescence lifetime for X-radiation generated exciplexes, and demonstrate its relevance for several typical systems.

Usually, exciplexes are observed by their emission, which is characterized by the position of the emission band, red-shifted with respect to the emission band of the parent luminophores, and by the fluorescence lifetime (τ_F). The τ_F value is defined as

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an average time that a species remains in an excited state prior to returning to the ground state by emitting a photon.[4] In most cases the τ_F value is not affected by inner filtration, static quenching, or changes in the luminophore concentration, which makes it a widely used experimentally measured parameter to characterize a luminophore or exciplex.

Several methods exist to determine the τ_F value of a luminophore, which can be divided into time-domain[5] and frequency-domain[6] categories. In the first case the time-dependence of the emission intensity after pulsed excitation of the luminophore is registered. The obtained kinetics of fluorescence is fitted by a sum of exponentials, whose characteristic time constants yield the τ_F values. The longest lifetime, typically associated with exciplexes, visually reveals itself as the long-time tail of the kinetics and can be directly evaluated. In the second case the sample is excited with continuous wave (CW) radiation with a modulated intensity, and the time dependence of the CW fluorescence intensity is measured and analyzed. Due to the technical complexity,[7] the frequency domain methods are not widely spread, while direct and clear in visualization time-domain methods became a routine way for fluorescence lifetime measurements.

In the case of optical excitation the observation of exciplexes requires to meet three necessary conditions: (I) acceptable optical density of the sample at the excitation wavelength, (II) sufficient τ_F value of the luminophore to form the exciplex in a bulk reaction with the partner and (III) spectral separation of the absorption bands of the two partners if selective excitation of one of them is desired. For donor–acceptor systems discussed in this work and for experimental conditions typical for radiation chemistry, each of these three conditions is normally not met. A rare exclusion is the anthracene–DMA pair, which effectively generates exciplexes under both X-rays and optical radiation. This pair was used in the present work to calibrate the proposed method of the exciplex lifetime estimation.

In the case of X-ray excitation the measurements of the exciplex τ_F value by time-resolved methods are not straightforward. The formation of exciplexes under X-radiation proceeds *via* geminate recombination of radical ion pairs resulting in a non-exponential kinetics of recombination luminescence. The latter is a convolution of the kinetics of recombination and deactivation of the formed excited species, and is characterized by strong evolution with time. At the initial stage, at times of the order of a few nanoseconds, the recombination rate significantly exceeds the rate of radiative decay of electronically excited species. At long times the recombination kinetics is described by a universal power-law that typically obscures the exponential decay of the excited states. Determination of fluorescence lifetimes from kinetics requires a numerical modeling of experimental curves, with the reaction scheme including dozens of reactions with their corresponding parameters, the values of which have to be estimated independently. Although a complete analytical solution for the geminate recombination kinetics is available,[8] it is extremely awkward. Furthermore, for practical modeling the kinetics has to be convolved with the distribution of ion pairs over the initial distances. The determination of this function is a separate problem in radiation chemistry.

In rare exceptions the τ_F values for X-radiation generated exciplexes could be determined using an approximately exponential fragment of kinetics between the very fast and very slow parts of the recombination luminescence without analyzing the entire kinetics. The main problem of this estimation is a strong contribution from the excited states of luminophores. Modeling demonstrates[9] that except for special cases the main contribution to this part of the kinetics comes from direct excitation transfer from excited solvent molecules to luminophore molecules. This channel overbears any possible contribution from the exciplex channel even when detecting in the exciplex emission band due to a large number of solvent excitations, high emission quantum yield of any normal luminophore, and always having partial overlap of the exciplex and intrinsic luminophore emission bands. Thus, such estimations are possible only for systems with low quantum yields and short τ_F values for luminophores, or with spectrally well-separated emission bands of luminophores and exciplexes. In this work we found a system, the diphenylacetylene–DMA pair, for which the exciplex τ_F value could be estimated directly from the recombination luminescence kinetics because of the ultrafast decay of the diphenylacetylene excited state (8 ps).[10,11]

Another standard experiment used for τ_F determination is physical or chemical quenching of the emission by varying the concentration of a quencher. The slope of the Stern–Volmer plot of the relative quenching efficiency $I_0/I - 1$ *vs.* the quencher concentration gives the product of τ_F and the rate constant of the quenching reaction k_d (typically diffusion-controlled). Usually in these experiments τ_F is known and k_d is determined. This approach has also been used to measure the concentration of dissolved oxygen by quenching of exciplexes with known lifetimes.[12,13] However, if the Stern–Volmer plots are used to determine the lifetime of an exciplex, the rate constant of its quenching reaction must be known, which is certainly not the case for a previously unknown exciplex. Thus, the absolute exciplex τ_F values could not be determined without the knowledge of k_d.

To the best of our knowledge, there is no conventional method to determine the fluorescence lifetimes for exciplexes formed under X-radiation. The existing approaches are suitable only for special cases but not in general. In the present work we suggest a simple and universal method to estimate the τ_F values for X-radiation generated exciplexes from arbitrary donor–acceptor pairs. The method is based on comparing the degree of dissolved oxygen quenching of the emission intensity for the exciplex and a luminophore with a known excited state lifetime. The key point of the proposed approach is the assumed similarity of the quenching rate constants for the exciplex and luminophore under the same conditions. Using this approach the τ_F values were estimated for four donor–acceptor pairs, and as a check for three of them the same values were obtained by different conventional methods. A good agreement in the τ_F values obtained by several methods supports the validity of the proposed approach.

2. Reaction scheme

Exciplexes in nonpolar solutions are usually generated *via* a bulk reaction of an electronically excited molecule, produced by optical illumination in its absorption band, with a partner molecule introduced in the solution.[14–18] Such photogenerated exciplexes form only in a limited number of special systems with one of the partners having an excited state lifetime sufficient for the required bulk reaction with the other component at acceptable optical densities of the solution and thus quencher concentrations. Some typical examples are certain donor–acceptor systems in alkanes,[19,20] such as pyrene–DMA[21,22] and anthracene–DMA[23] in alkanes. In polar and weakly polar solvents upon optical excitation exciplexes form as intermediates in the process of electron transfer, *e.g.*, from donor to singlet electronically excited acceptor molecules.[24,25] Exciplex luminescence in this case is mostly studied in the context of magnetic field effects in the emission band of the generated excited complexes.[26,27] Typical donor–acceptor pairs for such experiments are pyrene or anthracene as the acceptor with aromatic amines (*e.g.*, DMA) as the donor.[28–35]

Under radiation of X-range, the ionization of the solvent (1, the numbers refer to Scheme 1) yields the solvent radical cation (hole, $S^{+\bullet}$) and electron, which efficiently recombine due to Coulombic attraction with the formation of an excited solvent molecule S^* (2). In the presence of an electron acceptor A and electron donor D, a radiationless energy transfer from S^* can produce the excited donor D^* or acceptor A^* molecules (3A, 3B). Acceptor A and donor D can also compete with recombination (2) for holes and electrons: compounds with an ionization potential (IP) lower than IP of the solvent molecule (*e.g.*, various amines) can capture holes (4A) and compounds with sufficient electron affinity (*e.g.*, hexafluorobenzene and other fluoroorganic compounds) capture electrons (4B). Certain compounds can capture both holes and electrons (*e.g.*, *p*-terphenyl, anthracene and other polyarenes). The electron capture by acceptor A (4B) decreases the rate of recombination (2) and increases the probability of secondary radical cation formation. In most cases reactions (4A) and (4B) are diffusion-controlled. Since in nonpolar solutions the electron mobility
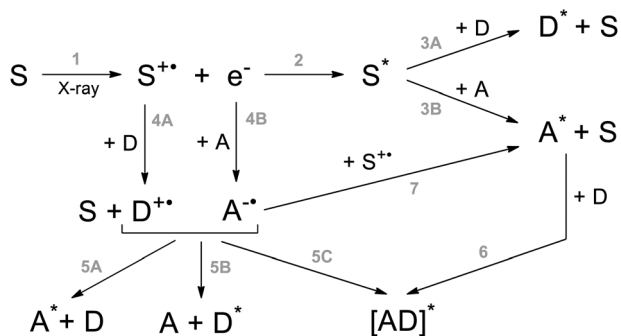
exceeds the hole mobility by two orders of magnitude, a comparably efficient electron and hole capture requires significantly higher concentrations of donor D, and typically used concentrations of A and D are at the level of 10^{-4} M and 10^{-2} M, respectively. Recombination of the secondary radical ion pairs $A^{-\bullet}/D^{+\bullet}$ in nonpolar solutions occurs with almost 100% efficiency at the first encounter of the mutually attracted radical ions and proceeds *via* reactions (5A–C). The products of the reactions (5A–C) are the electronically excited molecules A^* or D^* both in singlet and in triplet states and exciplexes [AD]*. Also under X-radiation exciplexes [AD]* can be formed *via* a bulk reaction (6) analogously to the case of optical generation of exciplexes. Formation of A^* can proceed both *via* reaction (3) and *via* recombination of other radical ion pairs present in solution (7).

The major advantage of X-radiation generation of exciplexes is its independence on the lifetime of the acceptor excited state A^*. As a result, exciplexes can be efficiently formed for systems with short excited state lifetimes of acceptors, such as *p*-terphenyl (0.95 ns)[36] or diphenylacetylene (8 ps).[10,11] The listed set of key reactions is sufficient to describe the processes under the conditions of steady-state sample irradiation with a relatively low dose rate of X-rays as used in this work.[37] A more detailed scheme of radiation-induced processes in solutions, including reactions and species required to describe track evolution at early times, can be found, *e.g.*, in ref. 9 and 38–40.

A scheme of exciplex formation similar to that described above was earlier suggested for excimers of pyrene (τ_F = 370 ns)[41] under X-radiation of nonpolar solutions.[42,43] Several studies earlier reported exciplexes generated by pulse irradiation of various polymeric systems,[44,45] as well as typical donor–acceptor systems accessible for optical excitation.[46] Excimer formation for *trans*-stylbene, diphenylacetylene, naphthalene and several other aromatic hydrocarbons was reported upon heating of γ-irradiated glassy samples in an *o*-terphenyl matrix pre-cooled to 77 K (ref. 47–49) and was ascribed to the preformed dimeric radical cations that recombined with their counter-ions when the mobility was thawed upon heating. Excimers of noble gases were also reported in experiments on pulse radiolysis of supercritical xenon,[50] as well as excitation of noble gases with synchrotron radiation.[51] Still, all these studies did not provide a method yet to evaluate τ_F for optically inaccessible exciplexes in solutions generated *via* pair recombination.

Another route to exciplex generation is electrogenerated chemiluminescence (ECL), when oppositely charged radical ions are generated in solution at electrodes.[52–55] Upon encounter they form an encounter complex, electron transfer in which can produce an exciplex. In this case the limiting factor for exciplex formation is the lifetime of the radical ions, as at least one of them must reach a substantial distance to meet its partner. Electrochemical generation in solution requires sufficiently polar media ($\varepsilon > 5$) with added supporting electrolyte to improve the radical ion stability.[56] An important advantage of ECL is its ability to generate electronically excited states that cannot be directly populated using optical excitation,

Scheme 1 Scheme of exciplex formation under X-radiation of a nonpolar solvent (S) containing an electron donor (D) and an electron acceptor (A) molecule.

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such as triplet states of benzophenone,[57] 10-methyl-phenothiazine,[58,59] 9,10-diphenylanthracene and rubrene.[60,61] ECL is also capable of generating excited complexes that are not directly accessible to optical excitation, *e.g.*, in systems of various acceptors (benzophenone anthracene, *etc.*) with tri-*p*-tolylamine in tetrahydrofuran.[62,63] Finally, electrochemical generation of exciplexes from molecules with rapid excited state deactivation, such as *p*-terphenyl,[64] as well as generation of the excimeric benzophenone radical anion that cannot be obtained *via* optical generation have been reported.[56] However, although ECL allows obtaining certain optically inaccessible exciplexes, it still cannot be used directly for their kinetic characterization in the nanosecond time range.

3. Experimental

Purified *n*-dodecane was used as the solvent in all experiments. DMA (99%, Aldrich) prior to experiments was distilled over zinc powder collecting the 193–195 °C fraction. Chromatographic analysis combined with mass-spectrometry showed DMA purity more than 99%. Anthracene (>99%), naphthalene (99%), *p*-terphenyl (≥99.5%), and diphenylacetylene (98%) from Aldrich were used without purification.

The CW spectra of recombination luminescence were obtained with a Magnetically Affected Reaction Yield (MARY) spectrometer with spectral resolution of luminescence in the visible range (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.[65]

The samples were irradiated with a BSV-27-Mo X-ray tube (Svetlana, St Petersburg, Russia), 40 kV, 20 mA, or with a high-pressure Hg lamp DRSh-500 equipped with a double monochromator DMR-4. In the case of optical excitation the monochromator slits 1.0 mm/1.0 mm were used. Under these conditions, λ_{ex} = 290 nm, the excitation photon flux was <10^{15} quanta per second. In all experiments the emission spectra were recorded with detection monochromator slits 2.2 mm/2.2 mm (spectral resolution about 10 nm).

The samples were degassed using repeated freeze–pump–thaw cycles. All spectra were recorded in identical round ampoules 5 mm in diameter made from molybdenum glass, which produces no intrinsic luminescence under X-radiation, or from quartz in the case of short-wave optical excitation. The sample volume was 250 µL. Each X-ray generated luminescence spectrum is an average over eight scans. Intensities are given as arbitrary units corresponding to the output signal of the detector and are consistent for all spectra. Further details on the experimental procedure and the choice of ampoule material can be found elsewhere.[65]

Time-resolved experiments with optical excitation were performed on a commercial Edinburgh Instruments FLSP-920 spectrofluorometer using the Time-Correlated Single Photon Counting (TCSPC) unit. The time profiles were recorded at different wavelengths over the emission band following exci-

tation at 375 nm (diode laser EPL-375; full width at the half maximum 80 ps) with a spectral resolution of 5 nm. The discussed X-ray induced luminescence kinetics were obtained on a home-built nanosecond pulse spectrofluorometer.[66] The recombination luminescence was detected in the exciplex and intrinsic luminophore emission bands with bandpass filters ZS-8 (λ_{max} = 530 nm, 70% transmission band $\Delta\lambda$ = 480–600 nm) and UFS-2 (λ_{max} = 330 nm, $\Delta\lambda$ = 280–380 nm), respectively, using TCSPC. Details of the experimental procedure for X-ray induced time-resolved experiment can be found elsewhere.[67]

4. Results and discussion

4.1 The oxygen quenching procedure

The suggested method for estimating the fluorescence lifetime for X-radiation generated exciplexes is based on comparing the degree of dissolved oxygen quenching of the emission from the exciplex and a standard luminophore with a known excited state lifetime. We shall assume that the quenching of both exciplex and standard luminophore emission is a diffusion-controlled process as described by the Stern–Volmer equation:

$$k_d \cdot [O_2] \cdot \tau_F = \frac{I_0}{I} - 1 \qquad (1)$$

where k_d is the rate constant of the quenching reaction, $[O_2]$ is the concentration of dissolved oxygen, τ_F is the excited state lifetime for the corresponding species, and I_0 and I are emission intensities in the absence and presence of dissolved oxygen.

The main assumption of the proposed method is the similarity of the k_d values for the standard luminophore and exciplex. Then, experimentally measuring the ratio I_0/I under the same conditions for the standard luminophore and the exciplex (for a degassed solution and solution in equilibrium under a normal atmosphere), and using the known τ_F value of the standard luminophore, we can estimate the exciplex luminescence lifetime from the following simple proportion:

$$^{lum}\tau_F \sim \frac{^{lum}I_0}{^{lum}I} - 1, \quad ^{ex}\tau_F \sim \frac{^{ex}I_0}{^{ex}I} - 1 \qquad (2)$$

where the lum superscript indicates the parameters for the standard luminophore and the ex superscript refers to the corresponding exciplex values. For the standard luminophore we used a solution of naphthalene in *n*-dodecane, τ_F = 96 ns.[36] Naphthalene is a convenient reference luminophore, since it has the τ_F value similar to the expected lifetimes of exciplexes in the systems under study. The use of the suggested proportion (eqn (2)) lets us to avoid the discussion of the unknown mechanism of the excited state quenching by oxygen (assuming it to be the same for the reference and system under study), as well as the explicit description of the non-exponential kinetics of X-radiation induced recombination fluorescence. As we shall see in the following section, the τ_F values obtained by this approach are in good agreement with the values determined by other methods.
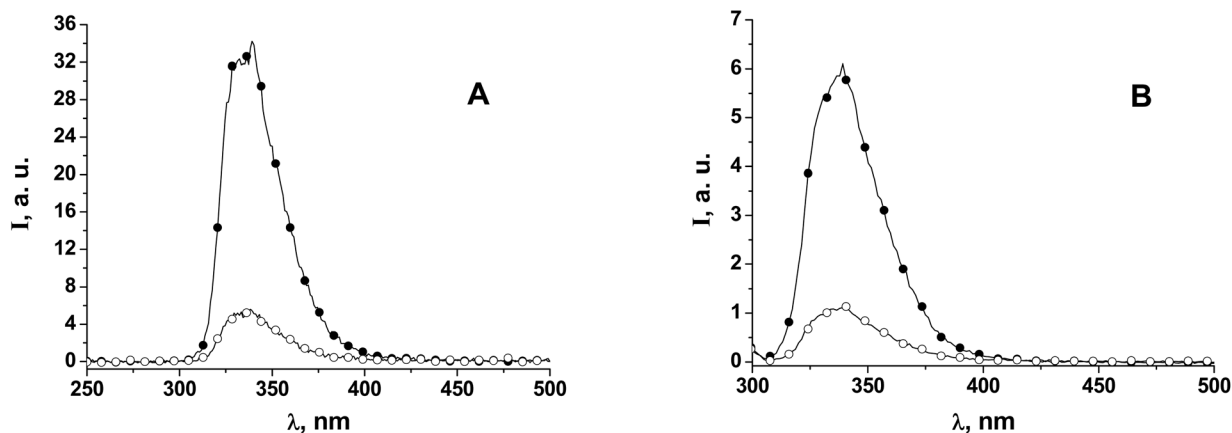
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Fig. 1 Emission spectra of degassed (●) and equilibrated under normal atmosphere (○) solution of 1×10^{-2} M naphthalene in n-dodecane under X-radiation (A) and 1×10^{-4} M under optical excitation at 290 nm (B). The integral quenching of the emission band $I_0/I - 1$ in the range 320 to 400 nm is 5.7 for X-radiation and 4.4 for optical excitation.

The dissolved oxygen quenching of naphthalene emission generated both under X- and UV-radiation is illustrated in Fig. 1. Under the same conditions the quenching is more pronounced under X-radiation compared with the optical excitation: $I_0/I - 1$ is equal to 5.7 and 4.4 for X-rays and optical excitation, respectively. The higher quenching efficiency is due to the additional multi-faceted interaction of oxygen with radical ion pairs. Dissolved oxygen can affect not only the luminophore excited state itself but also the processes leading to its formation, for example, the formation of secondary radical ions $A^{-\bullet}/D^{+\bullet}$ (reactions 4A and 4B, Scheme 1) and recombination of radical ion pairs (reactions 5A, 5B and 5C). Characteristic times of these processes can be tens of nanoseconds, and dissolved oxygen can suppress the excited state formation, $e.g.$, by capturing excess electron or quenching a radical ion. As a consequence of a more complex reaction scheme and the presence of an additional delayed stage susceptible to oxygen fewer excited states are formed in solution in the presence of oxygen and more efficient luminophore emission quenching is observed under X-ray irradiation. We assume that the effect of dissolved oxygen on the radical ion pairs $A^{-\bullet}/A^{+\bullet}$ and $A^{-\bullet}/D^{+\bullet}$ for naphthalene and its exciplex with DMA, respectively, is similar. Any further quenching of luminescence is determined by the lifetime of the excited state produced upon recombination and can be estimated from the Stern–Volmer equation (eqn (1)).

The spectra of X-radiation induced luminescence from degassed samples and the same samples under atmospheric pressure (dissolved oxygen concentration 2×10^{-3} M)[68] for donor–acceptor pairs anthracene–DMA, diphenylacetylene–DMA, naphthalene–DMA, and p-terphenyl–DMA in n-dodecane are shown in Fig. 2. In the case of anthracene (Fig. 2A), the emission from DMA (320–370 nm) was not observed because of its reabsorbtion by anthracene, present in the solution at relatively high concentrations and absorbing in the range of DMA emission. In Fig. 2B the corresponding spectrum for pure DMA (without addition of the "luminophore" proper) is

shown since diphenylacetylene produces virtually no intrinsic luminescence at this scale. Fig. 2C and D also show the spectra of radiation-induced luminescence from the luminophore and DMA, recorded under the same conditions without the second component of the mixture (DMA or luminophore, respectively). In all figures the red-shifted band observed for mixtures is the exciplex emission band.

The values of I and I_0 were obtained by integration of the spectra for two samples in the wavelength regions shown in Fig. 2. These integration regions were selected individually for each system to cover only the long-wavelength side of the total emission band corresponding to the exciplex emission without contribution from the intrinsic luminophore emission. The selection criterion for the correct integration range was the fact that the estimated exciplex τ_F value does not change with a shift of the initial integration point to a longer wavelength. I and I_0 values for each system were obtained from 4 to 6 independent experiments, their ratios were calculated for each experiment and then statistically evaluated. The resulting $I_0/I - 1$ values are listed in Table 1. The shown errors are the confidence intervals ($P_{con} = 0.95$) for the recorded set of experimental data.

The exciplex lifetimes were estimated according to the procedure described above, using the naphthalene excited state lifetime (96 ns)[36] as the reference. The obtained values are also listed in Table 1. The errors for exciplex lifetimes were calculated using the law of random error propagation. It should be stressed that exciplexes for all systems under study exhibit similar τ_F values in the range 50–70 ns despite a huge difference in the excited state lifetime of acceptors (from 8 ps for diphenylacetylene to 96 ns for naphthalene).

The observed large difference in the quenching of intrinsic luminophore and exciplex emission can be used to obtain the exciplex emission spectrum. As the quenching efficiency of the exciplex emission is higher than that of the intrinsic luminophore emission, a pure exciplex emission spectrum can be obtained by subtracting from the emission spectrum obtained
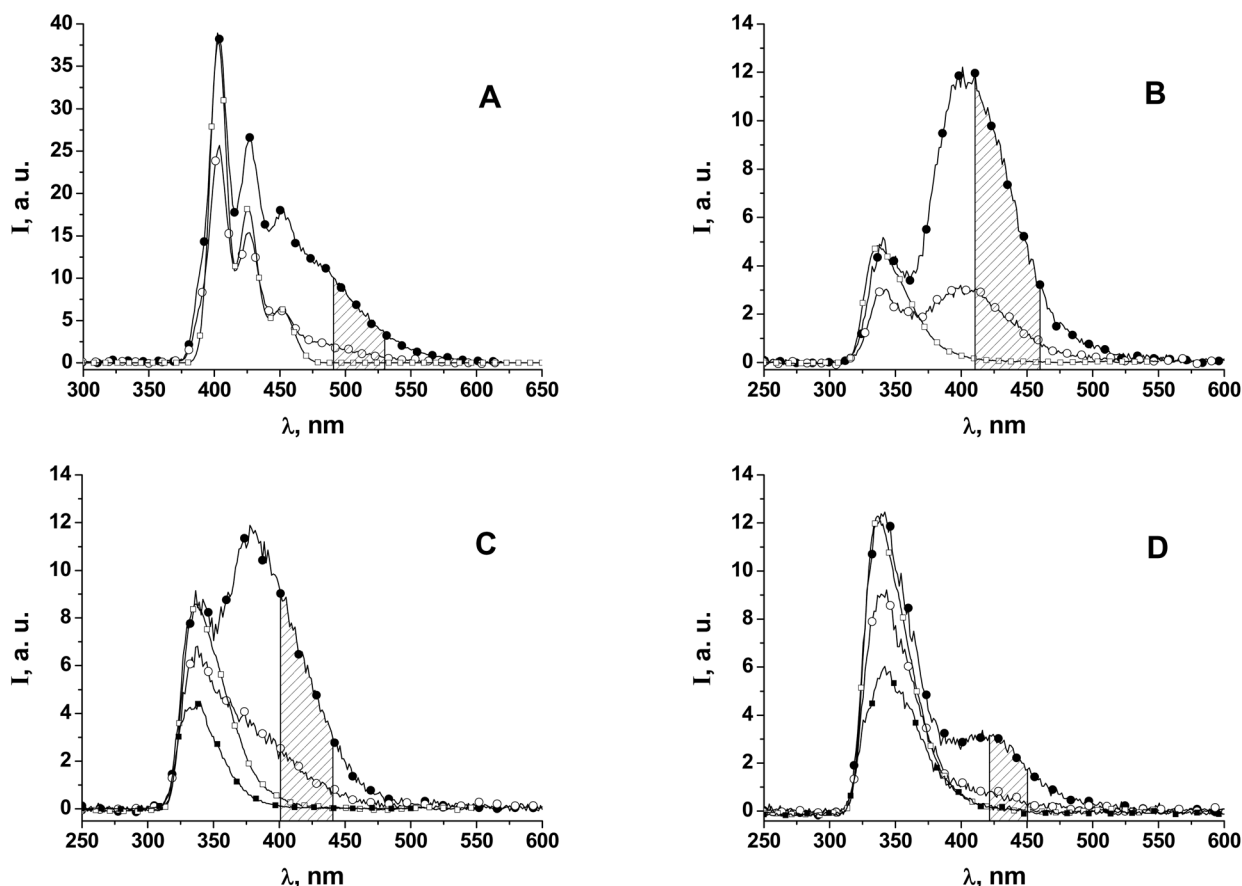
Fig. 2 X-ray generated luminescence spectra of degassed (●) and equilibrated under normal atmosphere (○) mixtures of A − 5×10^{-3} M anthracene and 1×10^{-2} M DMA; B − 1×10^{-2} M diphenylacetylene and 1×10^{-2} M DMA; C − 6×10^{-3} M naphthalene and 1×10^{-2} M DMA; D − 5×10^{-4} M p-terphenyl and 1×10^{-2} M DMA in n-dodecane. The four panels also show the following additional spectra for comparison: A − 1×10^{-2} M anthracene; B−D − 1×10^{-2} M DMA normalized to the maximum of the spectrum for the corresponding mixture, marked with (□); C − 1×10^{-2} M naphthalene; D − 8×10^{-4} M p-terphenyl normalized to half the maximum, marked with (■). The integral quenching of the exciplex emission band $I_0/I - 1$ in the indicated wavelength range is A − 4.3; B − 3.0; C − 3.2; and D − 3.9.

Table 1 The values of relative quenching $I_0/I - 1$ of the exciplex emission by dissolved oxygen and the estimated τ_F values for different exciplex-forming systems in n-dodecane

Optical excitation[a]		X-ray irradiation		
$\frac{I_0}{I} - 1$[b]	τ_F[b], ns	$\frac{I_0}{I} - 1$[b]	τ_F[b], ns	Exciplex-forming system
2.6 ± 0.3	56 ± 5	3.3 ± 0.1	54 ± 2	Naphthalene–DMA
—[d]	—[d]	3.9 ± 0.1	65 ± 2	p-Terphenyl–DMA
—[d]	—[d]	2.9 ± 0.1	49 ± 2	Diphenylacetylene–DMA
—[d]	72[e]	4.2 ± 0.2	70 ± 3	Anthracene–DMA
4.4 ± 0.1	96[c]	5.8 ± 0.1	96[c]	Naphthalene (reference)

[a] At 290 nm for naphthalene and naphthalene–DMA; at 375 nm for anthracene–DMA. [b] The confidence intervals ($P_{con} = 0.95$) were calculated from 4 to 6 independent experiments. [c] From ref. 36. [d] Not determined. [e] As determined from one time-resolved measurement.

in the absence of oxygen the emission spectrum for the same sample solution but obtained in the presence of oxygen. To completely get rid of intrinsic luminophore emission the emission spectrum obtained in the presence of dissolved oxygen

can be normalized to the maximum of the intrinsic luminophore emission intensity in the absence of oxygen. As an example Fig. 3 shows the emission spectrum of X-ray generated exciplexes for diphenylacetylene–DMA system obtained from the emission spectra of the same sample solution in the presence and absence of dissolved oxygen.

4.2 Comparison with conventional methods

4.2.1 Diphenylacetylene–DMA: recombination kinetics for a luminophore with a short intrinsic fluorescence lifetime. In donor–acceptor pairs with short lifetimes of the excited states of acceptors, $e.g.$, p-terphenyl (0.95 ns)[36] or diphenylacetylene (8 ps),[10,11] exciplex formation for used DMA concentration about 10^{-2} M under optical excitation is improbable. However, X-radiation turned out to be a universal method to generate exciplexes from such systems, and their emission can be followed both in CW ($vide\ supra$) and in time-resolved experiments. An efficient exciplex formation in p-terphenyl–DMA and diphenylacetylene–DMA pairs was demonstrated earlier[3,69] and proceeds via recombination of the radical ion

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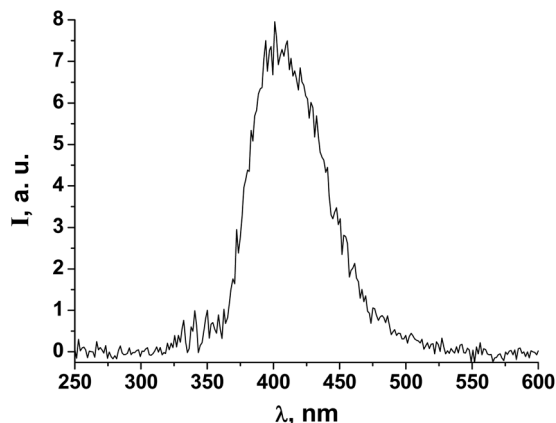This journal is © The Royal Society of Chemistry and Owner Societies 2016

Fig. 3 X-ray generated luminescence spectrum of the diphenylacety-lene–DMA exciplex obtained from the emission spectra of the same sample solution of 6×10^{-3} M diphenylacetylene and 1×10^{-2} M DMA recorded in the presence and absence of dissolved oxygen (see the text for description).

pair $A^{-\bullet}/D^{+\bullet}$ as shown in reaction (5C). Although CW experiments in this case are rather straightforward, the time-resolved studies of the kinetics of radiation-induced recombination luminescence are complicated by the non-exponential kinetics of geminate recombination with power-law tails and a complex set of reactions that need to be accounted for.[37] For example, a reasonably convincing description of the kinetics of X-radiation induced luminescence from N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) in alkane, being one of the simplest relevant systems, already includes 25 reactions.[9,38] The complexity of such modeling rapidly builds up with inclusion of the second acceptor, let alone exciplex formation.

However, an exciplex-forming system with a not emitting "luminophore" gives a rare chance to observe the exciplex emission evolution and to estimate the τ_F values without complete analysis of the kinetics. Fig. 4A and B display the kinetics recorded with the diphenylacetylene–DMA pair in n-dodecane for the blue and red sides of the total emission band (Fig. 2B), respectively. The presence of the long-lived signal (Fig. 4A and B) corresponding to the exciplex dynamics in both parts of the emission spectrum is due to the broad emission band of the exciplex completely covering the intrinsic luminophore emission band (Fig. 2B).

Because of the geminate nature of recombination all such kinetics have a universal $t^{-3/2}$ tail that completely obscures any exponential processes. However, the kinetics contain an approximately exponential region, 20–100 ns, presented in the insets of Fig. 4A and B. Kinetics corresponding to the exciplex emission band (Fig. 4B) is well reproduced with a single characteristic time constant of 42 ns, while kinetics for the intrinsic DMA band (Fig. 4A) requires two characteristic time constants 4 ns and 43 ns. The longer time constant apparently belongs to the exciplex. The shorter time constant could originate from either DMA ($\tau_F = 2.4$ ns),[36] or n-dodecane ($\tau_F = 4.2$ ns).[70] Thus the estimated τ_F value for diphenylacetylene–DMA

exciplexes reasonably agrees with the value obtained by the oxygen quenching method (Table 1). This value is also close to τ_F values for similar exciplex-forming systems accessible for photoexcitation (e.g., 33 ns for a naphthalene–triethylamine pair in alkanes).[71]

The described approach critically relies on the very small value of the fluorescence quantum yield of diphenylacetylene (0.00336).[72] In the case of other exciplex-forming systems this estimate of the exciplex lifetime is complicated by intrinsic luminescence from the electron acceptor/luminophore of the system. Electron acceptors other than diphenylacetylene, used in this work, as well as in almost any radiation chemistry study with fluorescence detection, have τ_F values comparable either to those of DMA (p-terphenyl, anthracene) or of exciplex (naphthalene), and have rather high fluorescence quantum yields (0.93, 0.36, and 0.23 for p-terphenyl, anthracene, naphthalene, respectively).[36] As described in the Introduction section, this strongly complicates matters and in practice makes this approach unusable for the majority of donor–acceptor pairs.

Fig. 4C and D show the oxygen quenching kinetics of recombination luminescence from the diphenylacetylene–DMA pair in n-dodecane recorded for the blue and red parts of the total emission band. The sample was in equilibrium under normal atmosphere (dissolved oxygen concentration 2×10^{-3} M).[68] It could be seen that the quencher completely removes the long-lived part of the kinetics, leaving only the initial dynamics at times up to about 100 ns. This dynamics is well described by exponential functions (see the insets of Fig. 4C and D) giving characteristic time constants of 3 and 15 ns for the DMA and exciplex bands, respectively. Using the known concentration of oxygen and assuming the exciplex quenching to be a diffusion-controlled process with $k_d = (8.4 \pm 0.7) \times 10^9$ M^{-1} s^{-1} for n-dodecane[10] (value for the electron transfer reaction from diphenylacetylene radical anion to 1,2-dibromoethane), the τ_F value for the exciplex would be estimated as 25 ns. The 1.7 times difference with the experimentally obtained τ_F value in the presence of oxygen (Fig. 4C and D) should be related to a higher reaction rate constant for the dissolved oxygen quenching of the exciplex. Indeed, O_2 in n-dodecane at room temperature has a significantly larger diffusion coefficient (4×10^{-5} cm^2 s^{-1}, interpolated from ref. 73) than 1,2-dibromoethane (1.4×10^{-5} cm^2 s^{-1})[74] which could result in the observed difference of the factor of two.

4.2.2 Anthracene–DMA: exponential decay dynamics of optically generated exciplexes. Most donor–acceptor pairs used in radiation chemistry are simple organic molecules with broad and featureless optical absorption spectra, which substantially overlap each other. An efficient formation of the radical cation of the pair requires high concentrations of the electron donor, DMA, at the level of 10^{-2} M. This practically rules out the possibility of selective optical excitation of the acceptor. However, anthracene is an uncommon exception from this rule. Of the four systems studied in this work, anthracene can be excited at wavelengths of no DMA absorption >350 nm. Furthermore, anthracene in n-hexane has $\tau_F = 5.9$ ns,[75] that is sufficient to generate exciplexes in a conven-

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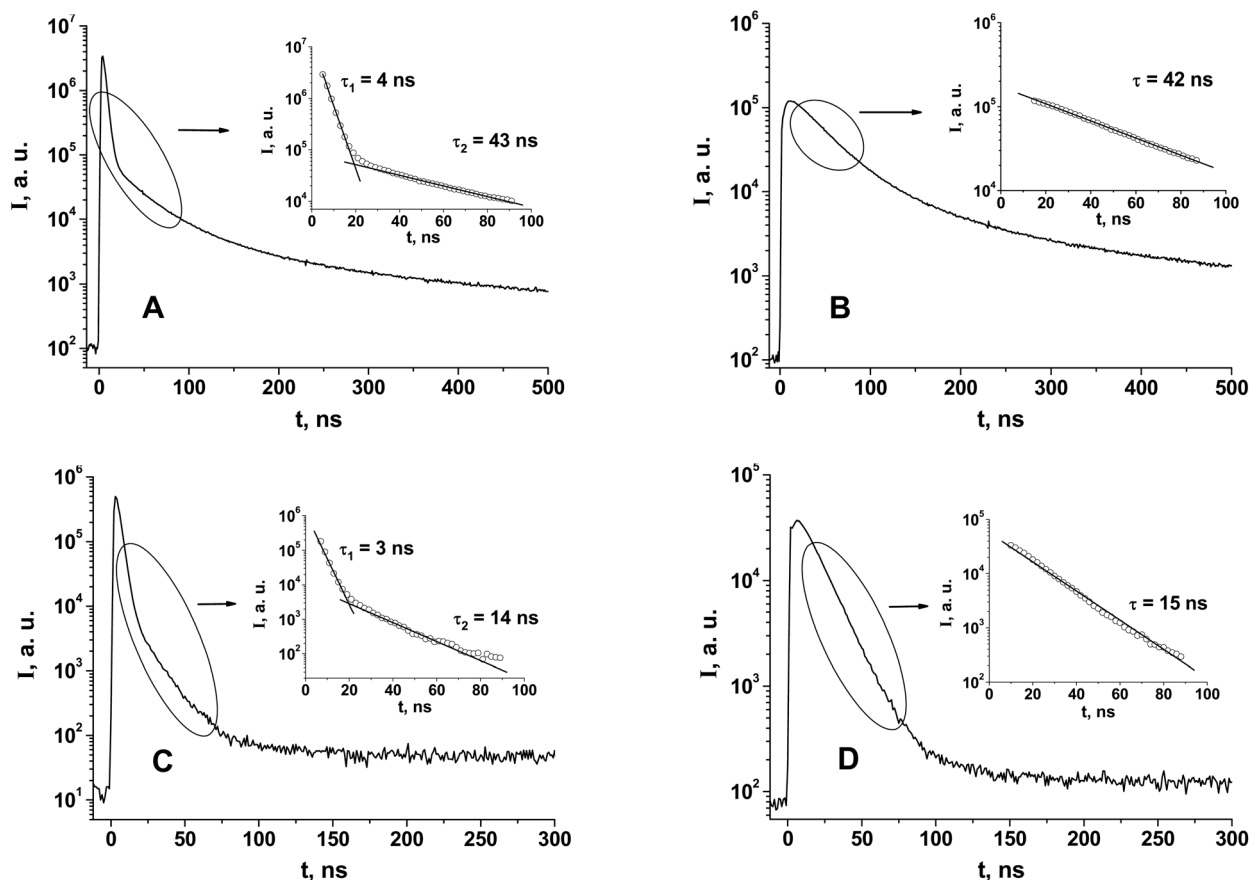*Photochem. Photobiol. Sci.,* 2016, **15**, 767–778 | **773**

Fig. 4 Kinetics of X-radiation induced luminescence for a degassed (A, B) and for an equilibrated under normal atmosphere (C, D) solution of 2×10^{-3} M diphenylacetylene and 1×10^{-2} M DMA in *n*-dodecane in the intrinsic luminophore (A, C) and the exciplex (B, D) emission band. The insets show exponential approximations of kinetics in the range 20 to 100 ns, yielding DMA and the exciplex emission lifetime in the absence (A, B) or in the presence of molecular oxygen (C, D).

tional way *via* a bulk reaction with its partner present at 10^{-2} M concentration. This gives us an opportunity to study this exciplex-forming system on a standard fluorometer under optical excitation.

Fig. 5 shows the kinetics of luminescence for a solution of anthracene and DMA in *n*-dodecane following excitation at 375 nm and detection at several wavelengths in the 480–600 nm range, covering the exciplex emission band (see Fig. 2A). The traces at longer wavelengths are well approximated with exponentials yielding $\tau_F = 72$ ns, which agrees well with $\tau_F = 70 \pm 3$ ns obtained from the oxygen quenching method (Table 1). These τ_F values are also consistent with the reported earlier fluorescence lifetime 77 ± 1 ns[76] for optically generated exciplex of anthracene–DMA in cyclohexane at 25 °C.

4.2.3 Naphthalene–DMA: dissolved oxygen quenching of optically generated exciplexes. The optical formation of exciplexes is possible only for two system considered in this work: anthracene–DMA ($\tau_F = 5.9$ ns for anthracene)[75] and naphthalene–DMA ($\tau_F = 96$ ns for naphthalene).[36] Although the former pair gives a possibility for selective excitation of the acceptor in the presence of a high concentration of donor, the naphthalene–DMA pair is a more typical example of systems used in
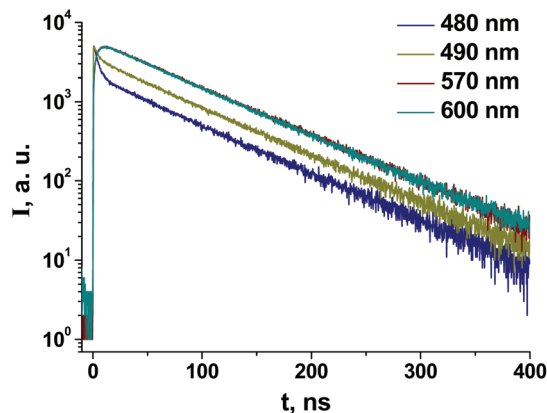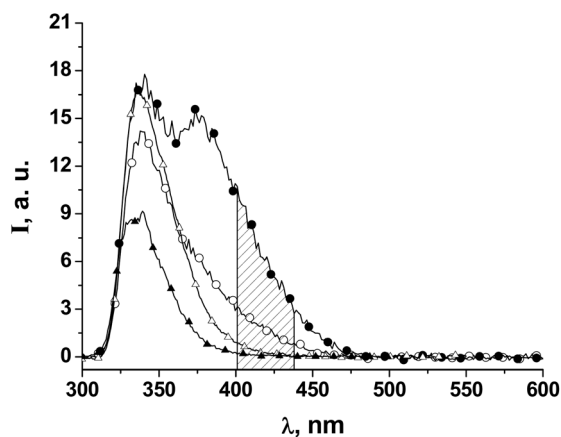

Fig. 5 Kinetics of photoinduced luminescence recorded with a bubbled with Ar solution of 5×10^{-5} M anthracene and 1×10^{-2} M DMA in *n*-dodecane at different wavelengths in the range 480 to 600 nm after the excitation at 375 nm.

radiation chemistry because of the substantial overlap of their absorption spectra.[36] In principle, DMA substitution by another amine could create a spectral window for selective

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excitation. For example, exciplexes of naphthalene with tri-ethylamine[71] and *N,N*-diethylaniline[19] have been optically generated *via* excitation of naphthalene. However, we would like to explore the more common situation of the overlapped spectra. Selective excitation of DMA is in principle possible, but not very useful because of its short-lived excited state (τ_F = 2.4 ns)[36] and an order of magnitude lower concentration of naphthalene, the partner in the required bulk reaction. Therefore it is easier to excite the solution in the region of naphthalene absorption overlapped with DMA absorption (we used mercury lamp line at 290 nm, extinction coefficients for naphthalene and DMA are 3200 M^{-1} cm^{-1} and 2200 M^{-1} cm^{-1}, respectively).[36] Due to high concentrations of naphthalene and DMA (6×10^{-3} M and 10^{-2} M, respectively), the optical density of the sample at the excitation wavelength was very high (about 9 for 0.25 cm ampoule). Under such conditions the incident light was absorbed in a thin layer and shared according to extinction coefficients of the components,[77] *i.e.*, mostly excited DMA molecules useless for exciplex formation are formed. However, as discussed in detail earlier,[3] exciplex formation in this system is still possible under optical excitation due to the long lifetime of the naphthalene excited state. Since a straightforward kinetic experiment on a commercial fluorometer could not be performed due to a very high optical density, we used the suggested oxygen quenching method with optical excitation.

The luminescence spectra were recorded with solutions of naphthalene and mixtures naphthalene–DMA in *n*-dodecane under optical excitation at 290 nm for degassed samples and the same samples in equilibrium under normal atmosphere (see Fig. 1B and 6). The spectra were taken in cylindrical quartz tubes with orthogonal geometry of the excitation and detection beams, so the emission was collected from the active layer. The procedure described in Section 4.1 for the estimation of exciplex τ_F values was performed for 4 to 5 pairs of independent experiments and statistically evaluated for each system. For naphthalene excited states the entire emission band was integrated to obtain the I and I_0 values, while for the naphthalene–DMA exciplex the range of 400–440 nm was used. The estimated τ_F = 56 ± 5 ns perfectly agrees with the value obtained for X-radiation (see Table 1).

4.2.4 *p*-Terphenyl–DMA: no alternative approach. The fourth system investigated under X-radiation, the *p*-terphenyl–DMA pair, is the most typical of the donor–acceptor pairs used in radiation chemistry. The acceptor, *p*-terphenyl, is a very efficient luminophore with a quantum yield of 0.93 and τ_F = 0.95 ns,[36] and is the default acceptor of choice in both CW and time-resolved experiments under ionizing radiation. The exciplex lifetime of 65 ns obtained by the suggested oxygen quenching procedure could not be verified by an alternative method because of the absence of special features exploited in the preceding Sections 4.2.1–4.2.3. The high fluorescence quantum yield results in a strong contribution from *p*-terphenyl excited states, generated by direct energy transfer from excited solvent molecules, in the exciplex emission even at the red side of the emission band (Fig. 2D). This makes impossible the recording of pure exciplex decay in the 20–100 ns time range used for the diphenylacetylene–DMA exciplex (Section 4.2.1). A short intrinsic fluorescence lifetime of less than 1 ns does not allow the exciplex formation at reasonable concentrations under optical excitation. However, the oxygen quenching method turned out to be as applicable in this case as for the other three systems covered in this work. The obtained τ_F value for the *p*-terphenyl–DMA exciplex (Table 1) agrees with the values determined in this work or known for other related systems. The described triple cross-check of the suggested method gives confidence of its reliability.

5. Conclusions

The suggested simple and universal method to estimate the fluorescence lifetimes of X-radiation induced exciplexes produces values in agreement with those obtained from time-resolved experiments under optical or X-ray excitation. This dissolved oxygen quenching method can be used for characterization of luminophores and other excited species formed under X-radiation. An important advantage of this method is to avoid the need for numerical evaluation of non-exponential kinetics of recombination luminescence described by a complex set of processes with poorly known parameters. Using this method we report the previously unknown fluorescence lifetimes for exciplexes of diphenylacetylene–DMA and *p*-terphenyl–DMA donor–acceptor systems in *n*-dodecane solution, which cannot be generated under optical excitation.

Fig. 6 Emission spectra of degassed (○) and equilibrated under normal atmosphere (●) mixture of 6×10^{-3} M naphthalene and 1×10^{-2} M DMA in *n*-dodecane under optical excitation at 290 nm. For comparison the emission spectra for 1×10^{-2} M DMA normalized to the maximum of the spectrum for the mixture and for 1×10^{-2} M naphthalene normalized to half the maximum are also given by (△) and (▲), respectively. The integral quenching of the exciplex emission band $I_0/I - 1$ in the range 400 to 440 nm is 2.6.

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