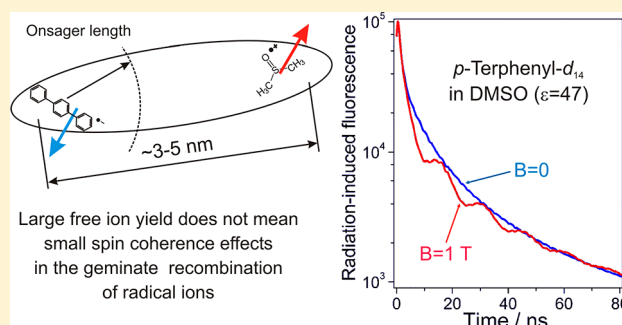Article

Unexpectedly Large Spin Coherence Effects in the Recombination Fluorescence from Irradiated Highly Polar Solutions on a Nanosecond Time Scale

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Ⓢ *Supporting Information*

ABSTRACT: Spin correlation effects in the geminate recombination of radical ion pairs in irradiated highly polar liquids are typically believed to be negligible due to a high escape probability for the ions. This report presents the results of an exploratory study of organic polar solvents aimed at the searching for, and estimating the magnitude of, the time-resolved magnetic field effects (TR MFEs) in the delayed radiation-induced fluorescence from diluted solutions of a luminophore. It has been found that upon the high-energy irradiation of the solutions in polar liquids, such as dichloroethane ($\varepsilon \approx 10$), methanol ($\varepsilon \approx 33$), acetonitrile ($\varepsilon \approx 37$), dimethylformamide ($\varepsilon \approx 37$), dimethyl sulfoxide ($\varepsilon \approx 47$), ethylene carbonate ($\varepsilon \approx 89$), substantial spin coherence effects in the delayed fluorescence can be observed within a time range up to ~100 ns. In most of the cases studied, magnetic resonance characteristics of primary or very early solvent-related radical ions were evaluated from the TR MFE curves. This approach can, therefore, be widely used to complement results obtained by the pulse radiolysis technique with structural and kinetic data extracted from the magnetic resonance characteristics of the short-lived radical ions formed in irradiated media.

Onsager length

~3-5 nm

Large free ion yield does not mean small spin coherence effects in the geminate recombination of radical ions

p-Terphenyl-d_{14} in DMSO (ε=47)

Radiation-induced fluorescence

B=0

B=1 T

Time / ns

INTRODUCTION

The purpose of this work is to present a new experimental opportunity to study processes involving molecules of a polar organic medium immediately after their ionization. This can be useful for improving, for example, the resistance of materials to high-energy radiation or the safety of batteries with organic electrolytes, whose components can be oxidized due to overvoltage.[1−3]

Actually, studies of radical ions are not simple due to the comparatively high reactivity of these particles, as well as their fast recombination with oppositely charged particles. As a universal method for studies of short-lived radical ions in solution, the method of pulse radiolysis is typically used because with high-energy radiation, any molecule can be ionized and excess electrons are easily created to reduce molecules of interest.[4,5] In addition, measurements of optical absorption provide high sensitivity and time resolution. On the other hand, the lack of structure and the overlap of optical absorption bands of the radiation-induced intermediates frequently cause serious difficulties in the interpretation of experimental data.

There is an alternative approach to investigate radical ions created in organic solutions by ionizing radiation. This is based on the spin coherence effects in the recombination fluorescence of radiation generated radical ion pairs (RIPs). The keystone of

the approach is that the primary geminate pairs "solvent radical cation/excess electron" are very probably to be in the singlet spin state at the moment of their formation. The spin coherence may be transferred to secondary RIPs formed via electron transfer reactions. If the fluorescence response of the irradiated solution is due, at least partially, to the recombination of geminate RIPs, then an external magnetic field, either constant or oscillating, may change the singlet state population of the RIPs ensemble and, consequently, the intensity of the radiation-induced fluorescence on a nanosecond or microsecond time scale. It is important that these changes depend on spin interactions of unpaired electron spins in both radical ions, which compose the spin-correlated RIP.

This principle was used to develop the stationary[6] and time-resolved[7] variants of the method of Optically (or Fluorescence) Detected Electron Paramagnetic (Magnetic) Resonance (OD EPR or FDMR), as well as the method of Magnetically Affected Reaction Yield spectroscopy,[8] that provide structural and kinetic information on radical ions in irradiated solutions. Typically, experiments are performed in solutions of a luminophore, which simultaneously is the acceptor of either positive or negative primary charge carriers depending on the

Table 1. Solvents Used in the Study, Their Dielectric Constants, and a Brief Description of the Results Obtained[a]

solvent	dielectric constant	delayed fluorescence	amplitude of TR MFE curves[b]	solvent-related charge carrier observed[c]
acetone[d]	21	yes	0.25[d]	solvent RA
N-methyl-2-pyrrolidone (NMP)	32	yes	0.2	?
N,N-dimethylformamide (DMF)	37	yes	0.15	?
acetonitrile (ACN)	37	yes	0.1	solvent RA
dimethyl sulfoxide (DMSO)	47	yes	0.4	solvent RC
propylene carbonate (PC)	65	yes	0.25	RC of dimer?[e]
ethylene carbonate (EC)	89 (40 °C)	yes	0.2	RC of dimer?[e]
methanol (MeOH)	33	yes	0.1	solvated electron
1,2-dichloroethane (DCE)	10.4	yes	0.1	solvent RC
chloroform	4.8	no[f]	0	-
hexyl aldehyde	9.5	no[f]	0	-

[a]Indication of the delayed fluorescence observability, TR MFE curve amplitude, and the proposed nature of the observed radical ions. [b]Maximal deviation from 1 for the TR MFE curves presented in Figures 2−5 (except for acetone). [c]Another radical ion in the RIP is formed from pTP molecule. [d]ref 20. [e]Complex between RC and molecule of solvent as suggested for irradiated PC;[21] [f]The radiation induced fluorescence drops off close to nearly background level within 10−20 ns after the pulse.

purposes of an investigation. The use of a luminophore, for which radical ionic states are well characterized, allows obtaining information on its counterion.

There is also a slightly different approach, referred to as the method of time-resolved magnetic field effect (TR MFE) in recombination fluorescence.[9,10] This exploits the comparison of the decay kinetics of recombination fluorescence intensity, measured at high ($I_B(t)$), i.e., substantially exceeding the ESR spectrum width of recombining radical ions, and almost zero ($I_0(t)$) magnetic fields. The comparison is performed by considering the $I_B(t)/I_0(t)$ ratio, which is referred to as TR MFE curve. At least in nonpolar media, this ratio appears to be nearly independent of intratrack RIP recombination rate, which rapidly decreases with time. This approach allows isolating small, ~10%, changes in the population of the singlet spin state of the RIP ensemble, while the recombination fluorescence intensity decays by orders of magnitude. It has been previously demonstrated that the TR MFE method allows one to extract the same spectroscopic information on short-lived radical ions as does EPR spectroscopy, i.e., to determine the g-factors, hyperfine coupling (HFC) constants, as well as the paramagnetic relaxation times of recombining radical ions.[11−13]

However, the above-mentioned spin chemistry approaches have mostly been used to study radical ions in irradiated solutions with a low polarity, where the probability of geminate recombination of spin-correlated RIPs tends to unity. Polar organic solvents were beyond the scope of these techniques although a screening study[14] has shown that FDMR spectra from secondary spin-correlated RIPs can, in principle, be observed in some ethers and alcohols with dielectric constant ε < 30.

Discussing the problem of studies of spin-correlated RIPs in polar media, we should mention the use of photoinduced charge separation to create the RIPs. In that case, absorption of an optical photon results in a closely spaced RIP, which typically is formed from the radical ions of solutes. The role of solvent, almost exclusively, is limited to a stabilization of the ions due to solvation. This approach has been applied by many research groups, and its possibilities and limitations have been discussed repeatedly in the literature (see, e.g., refs 15−17). However, independently of what is measured, for example, the yields of recombination products or the luminescence of exciplexes, the approach is limited regarding both the range of

accessible radical ions and the possibility of determining the magnetic resonance characteristics of these particles.

The present work demonstrates the previously unrecognized opportunities that are offered by the use of the method of TR MFE in recombination fluorescence for studying radical ions in polar, and even highly polar, media upon generation of the particles by high-energy radiation. Actually, the TR MFEs in such conditions have been observed earlier in ethers[18] and glymes,[19] having $\varepsilon \approx 7$. Very recently, striking magnetic field effects have been found in acetone ($\varepsilon \approx 21$)[20] and even in propylene carbonate ($\varepsilon \approx 65$).[21] These findings were initially considered as lucky exceptions, since Onsager radii, $R_O = e^2/(4\pi\varepsilon_0\varepsilon k_BT)$, in strongly polar media can be much less than initial distance between the primary charges created with a high energy radiation that greatly increases the geminate ion escape. Besides, it is usually believed that ionization of polar liquids, which are composed of molecules containing heteroatoms, is immediately, within picoseconds, followed by the proton or H atom transfer between the primary radical cations and surrounding molecules and, consequently, by the formation of independent particles, neutral radicals and cations (see, e.g., refs 4, 5, 14). Even if the recombination of a closed-shell cation with an anion would result in a fluorescence, no effects of magnetic field of the order of 1 T would be expected since spin selection effects could not take place in such ion pairs.

Nevertheless, the above-mentioned findings have stimulated carrying out an exploratory research involving a series of polar organic liquids to estimate (i) the upper limit of the solvent polarity, at which the spin coherence effects in the radiation-induced fluorescence from the luminophore solutions can be observed; and (ii) the chemical diversity of the solvents suitable for such observations.

■ METHODS AND MATERIALS

This research was performed using a series of the widely used polar organic solvents, listed in Table 1, which also summarizes the data on the observability of the delayed fluorescence and magnetic field effects from the diluted solutions of p-terphenyl-d_{14} (pTP) upon X-ray irradiation. para-Terphenyl molecules were chosen since they can form stable positive and negative radical ions and these exhibit a short, ca. 1 ns, fluorescence lifetime at high fluorescence quantum yield. For perdeuterated pTP, EPR spectrum widths are rather small and amount to $\Delta H_{pp} \approx 0.17$ mT for the radical anion (RA) and $\Delta H_{pp} \approx 0.19$

mT for the radical cation (RC), as evaluated on the basis of the data on HFC in the radical ions of the protiated compound.[22] Isotropic values of the g-factors of both these radical ions were assumed to be 2.0027 as for typical aromatic radical ions.[22] In acetonitrile solutions, as charge acceptor N,N-dimethylamino-tolan was also used. For this aromatic compound, EPR spectrum widths were previously estimated to be $\Delta H_{pp} \approx$ 0.74 mT for RA and significantly larger value, $\Delta H_{pp} \approx 2.4$ mT, for RC.[21]

N-Methyl-2-pyrrolidone (NMP, anhydrous, 99.5%, Sigma-Aldrich), N,N-dimethylformamide (DMF, anhydrous, 99.8%), chloroform (99%), hexyl aldehyde (98%, Sigma-Aldrich) were distilled before use. Dimethyl sulfoxide (DMSO, 99.9%) was distilled under vacuum. Methanol (MeOH, 99.9%) was additionally dried using magnesium turnings and acetonitrile (ACN, 99.8%, Aldrich) was additionally dried several times using P_2O_5 before the final distillation. 1,2-Dichloroethane (DCE, anhydrous, 99.98%), ethylene carbonate (EC, 99.9%), and propylene carbonate (PC, anhydrous, > 99.9%) were obtained, and the purity of these three liquids was guaranteed by the certificates of analysis from Sigma-Aldrich. p-Terphenyl-d_{14} (pTP, 98%, Sigma-Aldrich) was used as received. N,N-Dimethylaminotolan (DMAT, > 95%) was synthesized in the Voevodsky Institute of Chemical Kinetics and Combustion by O. M. Usov.

The freshly prepared solutions were degassed with several "freeze−pump−thaw" cycles.

Experimentally, we have studied the radiation-induced delayed fluorescence from nearly 1 mM pTP solutions in the mentioned solvents at room temperature, or at 40 °C for ethylene carbonate, in a magnetic field up to 1.8 T in oxygen-free conditions. The fluorescence intensity, $I_0(t)$ or $I_B(t)$, was excited by nearly 1 ns X-ray (~20 keV) pulses[23] with the absorbed dose of 10−100 nGy per pulse and was measured by means of single-photon counting within the wavelength range of 320−400 nm to isolate the pTP fluorescence.

To estimate magnetic resonance parameters of radical ions involved, some experimental TR MFE curves were compared with calculated ones. These trial calculations were carried out within the framework of the existing theoretical model developed for nonpolar liquids (see, e.g., refs 10, 11). Particular formulations can be found in the Supporting Information (SI). The model used is based, in particular, on the assumptions that (i) the ion recombination is irreversible; and (ii) the recombination probability for both singlet and triplet RIPs (other things being equal) is the same. A proof of the applicability of this model is not produced here. However, for some solvents, this is indirectly supported by an agreement with the experiment achieved.

■ RESULTS AND DISCUSSION

Figure 1 shows $I_0(t)$ curves for some solutions under study. The kinetic curves for the omitted cases, except for hexyl aldehyde, are close to those for EC or NMP. The $I_0(t)$ curves are normalized to a maximum to emphasize the relative contribution of the delayed fluorescence at $t > 10$ ns. For the solvents studied, the fluorescence intensity at this time domain is maximal for DMSO but negligible for chloroform and hexyl aldehyde. In the latter two solvents, the recombination fluorescence is, probably, completely absent. For chloroform, it can be speculated that the pTP radical anion, even if formed, rapidly transfers the excess electron to the solvent due to the higher electron affinity of the latter. Considering the results on
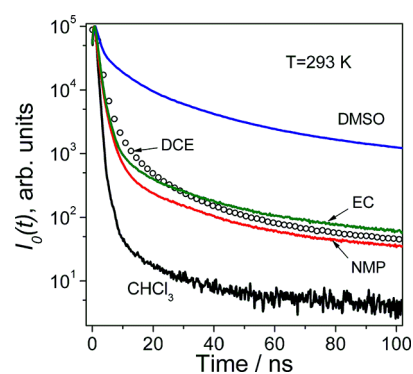

Figure 1. Time-dependence of the radiation-induced delayed fluorescence intensity $I_0(t)$ from 1 mM pTP solutions in (from top down at 80 ns) DMSO (blue), EC (green), DCE (circles), NMP (red), and chloroform (black).

dichloroethane and methanol (see below), the reasons why the solution in hexyl aldehyde exhibits no delayed fluorescence remain unclear.

In this work, the reasons why the observed $I_0(t)$ dependences in other solvents vary significantly are not discussed since it would require extensive considerations of many factors. The focus is on the results of the experimental TR MFE measurements shown in Figures 2−5 as well as on the
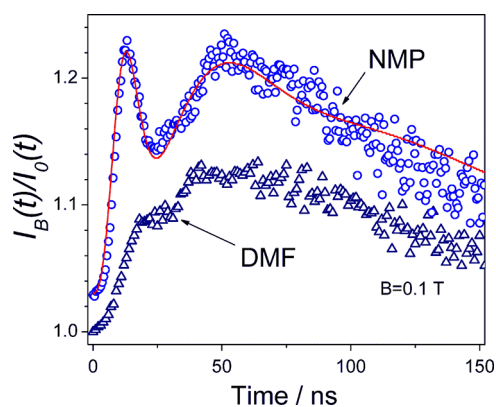

Figure 2. Ratios, $I_B(t)/I_0(t)$, of the radiation-induced fluorescence decays at $B = 0.1$ T and zero magnetic fields, respectively, at 293 K for 1 mM solutions of pTP-d_{14} in N-methyl-2-pyrrolidone (circles, shifted up by 0.03) and N,N-dimethylformamide (triangles). Red line shows the calculated TR MFE curve for NMP obtained assuming that there are two types of RIPs with almost equal contributions to the fluorescence intensity. In each pair, one of the partners is a pTP radical ion while its counterion is a radical ion with $\Delta H_{pp} = 1.5$ mT or $\Delta H_{pp} = 0.3$ mT (for a complete set of the parameters, see SI).

information, which can be extracted from these curves. These figures also present the results of above-mentioned trial simulations of the curves in the cases when such modeling is simple to perform without going into details of secondary importance. The most relevant modeling parameters are given in the figure captions. Other details can be found in the SI.

In all the cases where the delayed fluorescence has been detected, the noticeable time-resolved magnetic field effects have also been observed. Apparently, the most important result of this work is that these effects may be significant in amplitude and they may last long enough to visualize the evolution of the spin state of the RIPs ensemble created by the radiation pulse, even in highly polar media. With proper models, the TR MFE

curves can be used to determine the magnetic resonance characteristics of the observed radical ions. Further, TR MFE results obtained with particular solvents are discussed.

NMP and DMF. A particular feature of the TR MFE curves obtained with solutions in DMF and in NMP (Figure 2) is the evident manifestation of HFC in radical ions, whose recombination results in the observed fluorescence. This can be concluded from the presence of a relatively steep positive slope (DMF) or distinct peaks (NMP) in the curves at $t < 20$ ns as well as from the absence of any noticeable dependence of the curves on the magnitude of a strong magnetic field B. Note that the TR MFE effects are very small as compared to the change of recombination intensity with time. That is why the contribution of the coherent spin evolution of RIPs could hardly be seen in the $I_0(t)$ curves presented on a semilogarithmic scale in Figure 1.

As shown in SI in more detail, the time position, τ, of the first peak in TR MFE curves gives the estimate of ΔH_{pp} value for those RIP partner, which exhibit larger ESR spectrum width, as $\sim18(\text{ns}\cdot\text{mT})/\tau(\text{ns})$. This allows one to conclude without a thorough analysis that in the irradiated NMP solution a radical ion with $\Delta H_{pp} \sim 1.5$ mT is formed after the ionizing pulse without a noticeable delay. Evidently, this should be a solvent-related radical ion.

More accurate modeling of the TR MFE curve, as shown for NMP in Figure 2, suggests that there are two types of RIPs with almost equal contributions to the fluorescence intensity. In each pair, one of the partners is a pTP radical ion, while their counterions are solvent-related radical ions with EPR spectrum width, ΔH_{pp}, equal to ca. 1.5 mT and 0.3 mT. However, the modeling result related to the radical ion with a smaller ΔH_{pp} value is rather uncertain since the experimental TR MFE curve is strongly affected by paramagnetic relaxation at $t > 70$ ns.

In the case of DMF solutions, no distinct TR MFE features were observed. One possibility is that the primary solvent-related ions in irradiated DMF are transformed to other radical ions with differing magnetic resonance characteristics on a time scale of ~10 ns that is the same scale, on which the HFC-related peaks could be expected. Such process would result in additional dephasing in spin dynamics of spin-correlated RIPs that, in turn, greatly complicates the analysis of TR MFEs. In this case, a much more sophisticated study involving, in particular, a quantum chemical analysis of possible radical ion transformation pathways, should be performed.

At the same time, on the basis of the TR MFE curves presented in Figure 2, it can be concluded that the primary RCs hardly contribute to the effects observed in NMP. If this were the case, the substantial spin density should be localized on a nitrogen atom that would result in the EPR spectrum width of the RC as large as, at least, several millitesla[24] and, correspondingly, in a much steeper slope of the TR MFE curves at short times. A degenerate electron exchange involving these radical cations could decrease the rate of singlet–triplet transitions,[10,11] but in this case, no distinct peaks in the TR MFE curve could be expected (see SI for more details).

ACN. For ACN solutions (Figure 3), the observed TR MFE curves can be described assuming that the initial RIPs, created by irradiation, are composed of partners having small EPR spectrum widths and are transformed into secondary RIPs with a characteristic time ca. 14 ns. The difference between the g-factors of the RIP partners is $\Delta g \approx 0.001$ for the initial pair and nearly zero for the subsequent one. Note that a local maximum in the TR MFE curve at $t \sim 5$ ns at $B = 1$ T (Figure 3), within
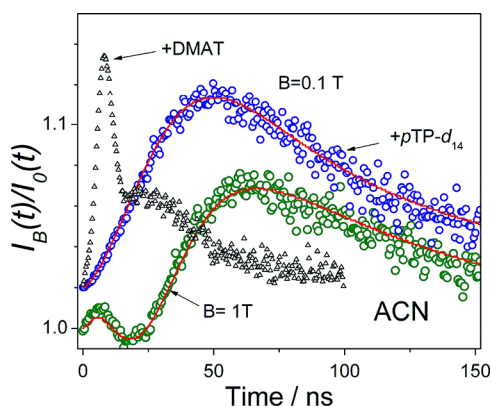

Figure 3. Ratios, $I_B(t)/I_0(t)$, of the radiation-induced fluorescence decays at high (indicated in the plot) and zero magnetic fields, respectively, at 293 K for 1 mM solutions of pTP-d_{14} (circles) and of dimethylaminotolan (DMAT, black triangles) in acetonitrile. Red lines show the calculated TR MFE curves assuming that both RIP partners have $\Delta H_{pp} < 0.1$ mT and the difference between their g-values amounted to 0.0009(1) (for a complete set of the parameters, see SI).

the frameworks of the used model, appears due to a slightly shorter paramagnetic phase relaxation time at zero field as compared to the strong field (see SI for more details).

The significant Δg value suggests that the earlier RIPs include a solvent-related radical ion. It can be supposed that this radical ion in the irradiated ACN is the primary or very early negative charge carrier, which, according to pulse radiolysis studies, exists at nanosecond time scales and can be scavenged by aromatic solutes with the rate constant of ca. 10^{11} M^{-1} s^{-1}.[25] This value of the rate constant just predicts the scavenging time ~10 ns at 1 mM concentration of pTP. Thus, it looks likely that the suggested subsequent RIPs are composed of the solute radical ions with similar g-factors.

This supposition is strongly supported by the results obtained with DMAT solutions in ACN (Figure 3). In this case, the TR MFE curve shows peak occurring at ca. 10 ns that corresponds to $\Delta H_{pp} \sim 2$ mT. The accurate simulation of this curve (not shown here) gives $\Delta H_{pp} \approx 2.4$ mT that agrees well with the estimated value of the EPR spectrum width of the DMAT radical cation.[21] It indicates that spin-correlated RIPs, which contribute to the fluorescence in 1 mM solution of aromatic solute, are composed of rapidly formed solute radical cations. The same can be expected also for the pTP solution. The corresponding counterion having significantly different g-value is, evidently, solvent-related negative charge carrier.

Of course, further studies are necessary to establish the nature of the radical ions detected in irradiated solutions in ACN. In particular, the TR MFE curve for DMAT solutions decays rapidly at $t > 30$ ns for unclear reasons, and this peculiarity impedes estimating the EPR spectrum width of the negative counterion in this solution that would be desirable to strengthen the interpretation. However, it is worth noting that the data on spin interactions in very early radical ions in the irradiated liquid amides or acetonitrile is reported for the first time (see, e.g., refs 25−27). This information should help in understanding the mechanisms of the primary radiation-chemical processes in these liquids.

DMSO and Carbonates. As for the cases shown in Figure 4a,b, the TR MFE method provides the possibility to interpret the results more or less unambiguously, even at this stage. Here, no substantial contribution of HFC was found, which allows
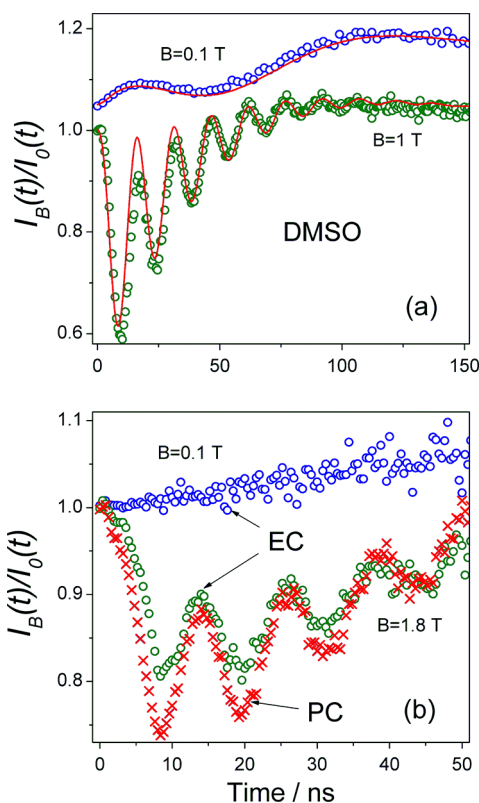
Figure 4. Ratios, $I_B(t)/I_0(t)$, of the radiation-induced fluorescence decays at high (indicated in the plot) and zero magnetic fields, respectively. Experimental data, which are shown by scatter plots, were obtained at 293 K for 1 mM solutions of pTP-d_{14} in (a) DMSO (curves related to $B = 0.1$ T are shifted up by 0.05); (b) ethylene carbonate (at 313 K, circles) and propylene carbonate (red crosses). Note the different scales on the time axes. Red lines in the plot (a) show the TR MFE simulation results at the difference between the g-values of recombining radical ions amounted to 0.0047(1) (for a complete set of the parameters, see SI).

the observation of nearly single frequency quantum beats in the singlet state population, caused by the difference between the g-factors of the RIP partners.[10]

In the case of the solution in DMSO (Figure 4a), the beat frequency corresponded to $\Delta g \approx 0.0047$ with a high accuracy. According to low-temperature studies of irradiated DMSO with the EPR spectroscopy,[28] the primary DMSO radical cations exhibit an isotropic value of the g-factor as large as 2.0074, which actually provides nearly the same Δg value relative to the pTP radical ion. Thus, we may assert with certainty that in this case fluorescence arises due to recombination of the "DMSO$^{\bullet+}$/pTP$^{\bullet-}$" pairs, facilitated by a relatively high rate of the formation of the solute radical anions in this solvent.[29] The HFC constant with protons in DMSO$^{\bullet+}$ is, very likely, averaged to a small value due to the fast electron exchange involving solvent molecules.

For the solutions in EC and PC (Figure 4b), the frequencies of the beats observed virtually coincide, i.e., the g-factors of the corresponding radical ions are very close to each other. In the recent communication,[21] the g-factor difference between recombining radical ions in irradiated pTP solution in PC has been determined to be as large as 0.0032. It was proposed that in irradiated liquid PC the carriers of both positive charge and unpaired electron spin are charged dimeric complexes of two solvent molecules with the spin density delocalized over two antiparallel carbonyl groups. The similarity between these two carbonates, PC and EC, is in agreement with that hypothesis. Note that the probability of geminate recombination in these highly polar liquids is not reduced to zero, since the RIP recombination radius is likely to remain appreciable, ~1 nm.[21]

DCE and MeOH. Figure 5a,b demonstrate the existence of the spin-correlated RIPs in systems in which it seems to be
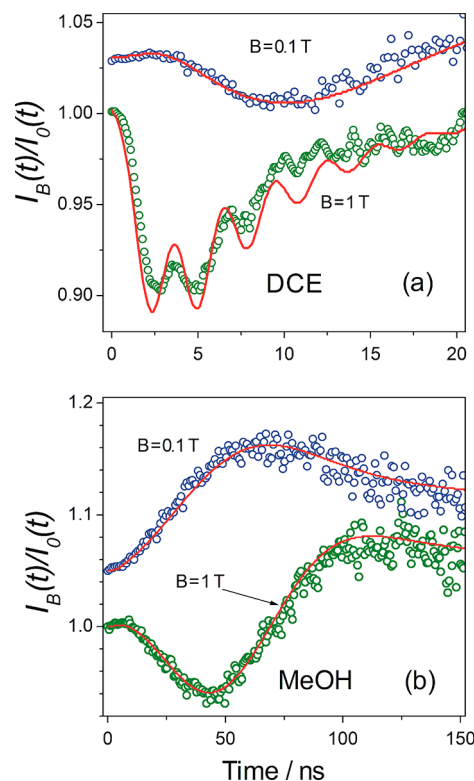

Figure 5. Experimental ratios, $I_B(t)/I_0(t)$, of the delayed fluorescence decays at high (indicated in the plot) and zero magnetic fields, respectively (scatter plots), as obtained at 293 K for 1 mM solutions of pTP-d_{14} in (a) DCE; (b) MeOH. Note the different scales on the time axis. Red lines in the plots show the TR MFE simulation results assuming the difference between the g-values of recombining radical ions amounted to 0.024(2) for DCE and 0.00053(2) for MeOH. Curves obtained at $B = 0.1$ T are shifted up.

improbable. One of these systems is the diluted pTP solution in DCE (Figure 5a). It is commonly believed that in chloroalkanes, the excess electron decays via dissociative attachment to a solvent molecule, forming chloride anion on a time scale of ~10 ps. Nevertheless, in the solution in DCE, both the delayed fluorescence and the TR MFE are observed, thus confirming the formation of spin-correlated RIPs including a solute radical ion. The TR MFE curves can be modeled assuming the Δg value for the RIP partners to be about 0.024. This value can be compared with data on the RC of 1,3-dichloropropane, for which the spin density on the chlorine atoms is almost the same as for the RC of 1,2-dichloroethane.[30] According to the cited work, the isotropic g-value of the 1,3-dichloropropane RC amounts to about 2.02, which suggests strongly that in irradiated pTP solution in DCE the delayed fluorescence arises from the recombination of the "DCE$^{\bullet+}$/pTP$^{\bullet-}$" pairs. The HFC in the chloroalkane RCs is averaged due to the fast degenerate electron exchange, as in the case of freons.[31] The small amplitude of the effects can be partially

explained by the fast paramagnetic relaxation in the radical cations ($T_1 \approx 10$ ns), which is probably to be caused by the modulation of the isotropic HFC by electron exchange, as well as of considerable anisotropy of the HFC- and the g-tensors by rotation.

The magnetic field effect was also observed for the diluted solution in methanol (Figure 5b). In this solvent, the primary RC is believed to decay instantly via a proton transfer reaction with surrounding solvent molecules.[4] Nevertheless, the spin-correlated RIPs are formed, which is confirmed decisively by the TR MFE observation. The experimental TR MFE curves can be modeled by assuming the EPR spectrum width of one of the partners to be negligibly small and the Δg value for the recombining radical ions to be 0.00053. Since the solvated electron, e_S^-, in methanol exhibits the g-value as large as ≈ 2.0021,[32] it can be concluded that the observed fluorescence is due to recombination of the "pTP$^{\bullet+}$/e_S^-" pairs.

In the cases studied, the noticeable TR MFEs were detected at times less than ~100 ns, while at longer times, the ratios reduce to 1. In the theory, as demonstrated in the SI section (Figure S1), such reduction takes place due to spin–lattice relaxation of the radical ions. However, the corresponding values of the "effective" relaxation times, T_1, which were obtained from the modeling, did not exceed 300 ns. Except for the case of DCE, there is no saying on this stage why these T_1 values are much shorter than typical T_1 values for free radicals that fall into microsecond time range in low viscosity solvents. It looks likely that this too rapid decay of the magnetic field sensitive fluorescence is not due to the spin–lattice paramagnetic relaxation. Since the delayed fluorescence intensity quickly decays with times (see Figure 1), it is probably that the recombination fluorescence becomes at $t > 100$ ns too weak against the background of a parasitic emission also generated by ionizing X-ray pulses. Note that such decrease in the contribution of spin-correlated RIPs to the fluorescence could partially account for the above-mentioned unobservability of the FDMR spectra[14] at $\varepsilon > 30$ since these spectra are formed mainly due to microwave-induced singlet–triplet transitions in the long-lived RIPs.

CONCLUSIONS

Finally, the results presented show clearly that high solvent polarity is not, generally speaking, an obstacle to observing spin coherence effects in the recombination of geminate RIPs generated by high-energy radiation. Even in the case of chemically unstable primary charge carriers, the probability of forming the solute radical ions in diluted solutions can be large enough to yield a detectable fluorescence from the secondary spin-correlated RIPs. Therefore, the TR MFE method can be considered as a much more universal approach than had been believed earlier. Unique structural and kinetic data, which can be extracted from the magnetic resonance characteristics of very early radical ions in irradiated polar liquids, as well as of their mixtures, would complement the results obtained with pulse radiolysis and make more clear mechanisms of the primary radiation events. A substantial widening of the range of liquids, which can be used in the TR MFE experiments as solvents, is of importance for studies of radical ionic states of other compounds, too. Previously, many organic molecules and polymers were considered to be inaccessible with this method because of very low solubility of those substances in nonpolar solvents. Now, it is clear that solvent can be, in principle, selected in such a way that concentration of solute would be

high enough to achieve rapid formation of the secondary radical ions of interest.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.7b08813.

Details of the model used to simulate experimental TR MFE curves with modeling parameters (PDF)

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