Photophysics of the galvinoxyl free radical revisited

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Abstract

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Photophysics of the galvinoxyl free radical revisited†

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The photophysical properties of the free neutral radical galvinoxyl were studied by a combination of femtosecond time-resolved spectroscopy and quantum chemical calculations. The electronic absorption spectrum is dominated by an intense band at 430 nm that is ascribed to the Dg,10 ← Dg transitions. Upon photoexcitation at 400 nm, the population of the Dg,10 states decays within less than 200 fs to the electronic ground state. This ultrafast internal conversion does not involve intramolecular modes with large amplitude motion as the measured dynamics does not show any significant dependence on the environment, but is most probably facilitated by a high density of electronic states of different character. Depending on the solvent, a weak transient band due to the galvinoxylate anion is also observed. This closed-shell species, which is fluorescent although its deactivation is also dominated by non-radiative decay, is generated upon biphotoionization of the solvent and electron capture. The ultrashort excited-state lifetime of the galvinoxyl radical precludes photoinduced disproportionation previously claimed to be at the origin of the formation of both anion and cation.

Introduction

Galvinoxyl (Chart 1) is a free organic radical of outstanding chemical stability: it can be isolated in pure form and solutions are known to be stable even in the presence of oxygen.1,2 This stability stems from both steric hindrance induced by the bulky tert-butyl groups and efficient delocalization of the unpaired electron all along the conjugated system. It is widely used as an EPR standard and serves as a radical scavenger/antioxidant, and, as such, it has numerous biological applications.3,4 Since its discovery by G. Coppinger,1 galvinoxyl and many of its derivatives have been studied extensively and electronic absorption,5 photoelectron,6 temperature dependent EPR spectra,5,7,8 magnetic properties,5,8,10 X-ray structure,11,12 and photolysis experiments13,14 have been published.

Galvinoxyl has a C2 rotational symmetry axis in crystals.11 The observed C(CH–C) bond angle at the methine carbon is 134° and the dihedral angle between the phenyl groups’ planes is 12°. Overall, the molecule does not deviate greatly from planarity.5 Delocalization of the unpaired electron over the whole aromatic system has also been evidenced in liquid solution via infrared15 and EPR spectroscopy16 and reproduced by quantum chemical calculations.10

The lowest energy transition observed in the electronic absorption spectrum is located at 860 nm (1.4 eV),5 in agreement with CNDO/5 quantum chemical calculations that found the lowest excited state at the same energy.17 Galvinoxyl is a phenoxyl type radical and, apart from one publication18 about the fluorescence of 2,4,6-tris(tert-butyl)phenoxyl radical that has been questioned later on,19,20 no emission has been reported for this family of radicals. This is in contrast to, for example, the structurally similar diphenylmethyl type radicals, many of which emit around ~550 nm (2.3 eV) in room temperature solution.19,21

The diphenylmethyl radical itself has a temperature-independent and remarkably long excited-state lifetime of 260 ns22 and a high fluorescence quantum yield (\(\Phi_f = 0.3\)).23 This long lifetime is explained by the dipole forbidden character of the lowest transition reflected by a very low molar absorption coefficient.23 Weir and co-workers found that the excited-state lifetime of differently substituted and isotopically labeled diphenylmethyl radicals correlates well with the D1 state energy, as anticipated within the framework of the energy gap law.24 Likewise, the ketyl radicals derived from benzophenone are known to fluoresce in liquid solution at 298 K.19,25

Benzyl type radicals are also fluorescent (\(\lambda_f \approx 500\) nm), although only at low temperatures. The pronounced temperature effect on \(\Phi_f\) originates from vibronic coupling between the D1 and D2 excited states, which offers an efficient non-radiative...
decay channel once enough vibrational energy is available.\textsuperscript{19,22} Hence, the fluorescence lifetime at 77 K, where this channel is suppressed, amounts to 1.4 $\mu$s for the ππ D$_1$ excited state.\textsuperscript{22}

The appearance of the anion and cation emission bands at $\lambda_f = 590$ and 560 nm, respectively, upon UV irradiation of solutions of galvinoxyl has been ascribed to photoinduced disproportionation.\textsuperscript{13} Furthermore, a transient species with an absorbance maximum at $\sim 580$ nm observed in hexane and propanol solutions of galvinoxyl after UV excitation was ascribed to the excited state of galvinoxyl.\textsuperscript{14} From these measurements, the lifetime of the D$_1$ state was estimated to be on the order of tens of microseconds,\textsuperscript{14} an astonishingly high value considering that the D$_1$ state of galvinoxyl is, according to CNDO/S calculations, only 1.4 eV above its ground state.\textsuperscript{13} On the other hand, such a long lifetime agrees well with the occurrence of photoinduced disproportionation, which, as it involves the diffusive encounter of two galvinoxyl molecules, is only possible if the D$_1$ state of galvinoxyl is sufficiently long-lived.

We report here on a joint experimental and theoretical investigation of the excited-state properties of galvinoxyl in solution, using a combination of ultrafast spectroscopy and quantum chemical calculations. Unlike closed-shell molecules, radicals are characterized by a high density of relatively low electronic excited states. In the case of the galvinoxyl radical, the calculations presented here indicate that optical excitation at 400 nm (3.1 eV) leads to the population of the D$_0$ or D$_{10}$ state, a situation that is uncommon in closed shell molecules, where at most the second or third electronic excited state is reached at such excitation energies. We will show that, contrary to what has been previously reported, the excited-state lifetime of galvinoxyl is extremely short, in agreement with the high density of states, and with a lowest electronic excited state located only 0.9 eV above the ground state. Such a lifetime does not allow for the photoinduced disproportionation process previously suggested. The mechanism responsible for the formation of anion and cation will be discussed.

**Experimental and computational details**

Galvinoxyl (2,6-di-tert-butyl-3-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-p-tolyloxy free radical, also called Coppinger’s radical) was purchased from Aldrich and used as received. The solvents acetonitrile (MeCN), ethanol (EtOH), methanol (MeOH), toluene and cyclohexane were of analytical grade, purchased from Aldrich and used without further purification. Absorption spectra in the UV/ VIS spectral region were taken on a Cary 50 and in the NIR spectral region (up to 3000 nm) on a Cary 5000 spectrometer (Varian). Steady-state fluorescence was measured using a Cary Eclipse fluorimeter (Varian). The galvinoxyl radical samples for steady-state measurements had absorbances between 0.1 and 3 at 430 nm over 1 cm pathlength. Basic ethanol was obtained by adding 1% of aqueous NaOH solution to EtOH. The galvinoxylate anion samples had an absorbance of 0.8 at 580 nm since higher concentration improved chemical stability. Rhodamine B in ethanol ($\Phi_f = 0.7$)\textsuperscript{26} was used as reference to determine the fluorescence quantum yield.

The transient absorption (TA) setup has been described elsewhere.\textsuperscript{27,29} Excitation was performed at 400 nm (for galvinoxyl; derived from the laser fundamental by frequency doubling) or 580 nm (for galvinoxylate; obtained using a home-built 2 stage non-collinear optical parametric amplifier) with ca. 2–3 mJ cm$^{-2}$ pump energy ($\sim 1.5$ $\mu$J focused to 250 $\mu$m diameter) and spectral changes were monitored with white light pulses obtained by focusing weak 800 nm pulses into a CaF$_2$ window. The spectra were corrected for the chirp of the white light. The instrument response function (IRF) had a full width at half maximum (FWHM) of ca. 200 fs. The polarization of the pump was at the magic angle with respect to that of the probe pulses. The samples had an optical density around 0.2 at the excitation wavelength in the 1 mm pathlength cells used. During measurements, the sample solutions were agitated by nitrogen bubbling. No important sample degradation was observed as checked by steady-state absorption prior to and after the TA measurements.

At short times, when pump and probe laser pulse overlap, several non-linear effects can contribute to the measured signal, namely cross phase modulation (XPM), stimulated Raman and the coherent response. All but the latter can in principle be subtracted or singular value decomposition (SVD) can be used to separate them from the desired contribution resulting from a proper sequence of interactions with the pump and probe fields.\textsuperscript{30,31} Subtraction requires precise positioning and low sample concentration since XPM is a non-linear process. SVD is known to be hampered by spectral shifts.\textsuperscript{32} Because of these complications, we chose to perform a tail fit to the TA data ignoring those at time delays shorter than the width of the IRF. Obviously, this renders lifetimes of the order of the IRF inaccurate. The TA data have been analyzed by a multiexponential global fit and a target analysis.\textsuperscript{32} The latter assumes successive reactions transforming one “species” into another following exponential kinetic rate equations: $A_1 \rightarrow A_2 \rightarrow A_3 \rightarrow A_4$. Such an analysis yields so called evolution associated difference spectra (EADS) which are linear combinations of the decay associated difference spectra obtained in a global multiexponential analysis.\textsuperscript{32} The term evolution-associated is used to stress that EADS are related to spectral transformations that arise from either population dynamics (e.g. internal conversion) or vibrational and solvent relaxation. Since in the present case all these processes take place on the same time scale, it is in general not possible to unequivocally separate them and to assign a given EADS to a well-defined species.

Density function theory (DFT)\textsuperscript{33,34} and time-dependent DFT (TDDFT)\textsuperscript{35} have been used to characterize the isolated radical in the D$_0$ ground state. All calculations were performed with the ADF program package (ver. 2009),\textsuperscript{36} using a large triple-$\zeta$ polarized (TZP) basis set from the ADF Slater-type orbital (STO) basis set database and were run unrestricted.\textsuperscript{37} The ground-state geometry of galvinoxyl was thus optimized with the molecular symmetry constraint to C$_2$, with the 1s levels of the carbon and oxygen atoms frozen, and using the BLYP functional\textsuperscript{38,39} augmented with the Grimme’s semiempirical long-range dispersion correction (BLYP-D functional).\textsuperscript{40} To analyze the ground-state absorption spectrum of galvinoxyl, a TDDFT electronic excitation calculation\textsuperscript{35,41–43} was performed on the D$_0$ optimized geometry with the SAOP potential\textsuperscript{44,45} and the TZP basis set, targeting the 40 lowest-lying excited states of
The BLYP-D/TZP optimized ground-state geometry of galvinoxyl is non-planar with a predicted angle of 15° between the two rings. This value agrees well with the experimental X-ray structure value of 12°. The good agreement between experiment and theory actually extends to the whole structure, as attested for, for instance, by the similar values of the C–C–C bond angle at the methine carbon (calc. 134°, exp. 132°) and those of the C–O bond length (calc. 1.254 Å, exp. 1.20–1.27 Å).

The electronic absorption spectrum of the galvinoxyl radical in solution is shown in Fig. 1. This spectrum consists of an intense band around 430 nm and two weak bands at 770 and 860 nm. No other band could be distinguished at longer wavelength up to 3000 nm (data not shown). In MeCN and in basic EtOH solutions, an additional band not present in other solvents can be seen at 580 nm. The latter is not due to the galvinoxyl radical but arises from the galvinoxylate anion as discussed below. The TDDFT calculations performed with the galvinoxyl radical indicate that a high number of transitions of vanishing to very strong intensities contribute to this electronic absorption spectrum, as shown in Fig. 1. Table 1 summarizes the results of the electronic excitation calculation for the first 10 excited states Dn (n = 1, ..., 10). They consist in the predicted energies and oscillator strengths of the Dn ← D0 transitions, as well as their assignments based on the major monoelectronic excitation contributions and on the nature of the involved spin-up (π) or spin-down (β) Kohn–Sham spin-orbitals.

Since the differences in the shapes and energies of the π and β Kohn–Sham spin-orbitals are very small (see Table 1 and Fig. S3 in the ESI†), we will adopt here, for the sake of simplicity, the common HOMO (which is singly occupied for a radical) and LUMO notation. The most relevant π and β orbitals and energies are given in the ESI†.

The TDDFT calculations predict two electronic transitions lower in energy than that observed in the electronic absorption spectrum at 860 nm (Table 1). The corresponding D3 and D2 excited states are calculated at 1300 nm (0.9 eV) and 1200 nm (1.0 eV). These states have pure ππ character as they reduce each to a single monoelectronic excitation from one of the two β-spin-orbitals describing the oxygen lone pairs to the πHOMO (Table 1). They are predicted to have a negligible oscillator strength, in agreement with their absence in the absorption spectrum. The calculated 0.9 eV energy of the first state contrasts with former CNDO/S calculations that located this ππ transition at 2 eV and that found the first electronic state to be a ππ transition at 1.4 eV.17

The first observable electronic absorption band at 860 nm (1.4 eV) is thus assigned to the D1 ← D0 transition. This band as well as that at 770 nm, that can be ascribed to the D2 ← D0 transition, both have ππ character. The intense absorption band measured at 430 nm (2.9 eV, ε = 2.10^5 L mol⁻¹ cm⁻¹)5,13 is found to be due to both D0 ← D0 and D10 ← D0 transitions, which are predicted to occur at 2.5 eV (490 nm) and 2.6 eV (480 nm) and exhibit an admixture of ππ and ππ characters (Table 1 and Fig. 2).

The intense structured band with a maximum at 580 nm present in air saturated MeCN and basic EtOH can be ascribed to the galvinoxylate anion.13,47 The mechanism

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**Table 1** Calculated transition energies $E$ of galvinoxyl together with oscillator strength $f$, $\chi$ = main character (see also Table S1 in the ESI)

<table>
<thead>
<tr>
<th>State</th>
<th>$\chi$</th>
<th>Simplified MO ← MO transitions</th>
<th>Contribution (%)</th>
<th>$E_{\text{calc}}$/eV (nm)</th>
<th>$f_{\text{calc}} \times 10^4$</th>
<th>$E_{\text{exp}}$/eV (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>$^2\text{B}$</td>
<td>ππ</td>
<td>HOMO ← HOMO−1</td>
<td>100</td>
<td>0.929 (1300)</td>
<td>1</td>
</tr>
<tr>
<td>D2</td>
<td>$^2\text{A}$</td>
<td>ππ</td>
<td>HOMO ← HOMO−2</td>
<td>100</td>
<td>0.971 (1200)</td>
<td>0</td>
</tr>
<tr>
<td>D3</td>
<td>$^2\text{B}$</td>
<td>ππ</td>
<td>HOMO ← HOMO−3</td>
<td>66</td>
<td>1.509 (820)</td>
<td>261</td>
</tr>
<tr>
<td>D4</td>
<td>$^2\text{B}$</td>
<td>ππ*</td>
<td>LUMO ← HOMO</td>
<td>34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D5</td>
<td>$^2\text{A}$</td>
<td>ππ</td>
<td>HOMO ← HOMO−4</td>
<td>99</td>
<td>1.705 (730)</td>
<td>133</td>
</tr>
<tr>
<td>D6</td>
<td>$^2\text{B}$</td>
<td>ππ</td>
<td>HOMO ← HOMO−5</td>
<td>99</td>
<td>1.705 (730)</td>
<td>34</td>
</tr>
<tr>
<td>D7</td>
<td>$^2\text{B}$</td>
<td>ππ*</td>
<td>LUMO ← HOMO−1</td>
<td>100</td>
<td>2.383 (520)</td>
<td>0</td>
</tr>
<tr>
<td>D8</td>
<td>$^2\text{A}$</td>
<td>ππ*</td>
<td>LUMO ← HOMO−2</td>
<td>100</td>
<td>2.427 (510)</td>
<td>4</td>
</tr>
<tr>
<td>D9</td>
<td>$^2\text{B}$</td>
<td>ππ</td>
<td>LUMO ← HOMO−1</td>
<td>100</td>
<td>2.519 (490)</td>
<td>0</td>
</tr>
<tr>
<td>D10</td>
<td>$^2\text{B}$</td>
<td>ππ*</td>
<td>LUMO ← HOMO</td>
<td>32</td>
<td>2.530 (490)</td>
<td>4045</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ππ*</td>
<td>LUMO ← HOMO−2</td>
<td>48</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ππ</td>
<td>HOMO ← HOMO−3</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ππ*</td>
<td>LUMO ← HOMO−1</td>
<td>29</td>
<td>2.594 (480)</td>
<td>4405</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ππ</td>
<td>HOMO ← HOMO−3</td>
<td>15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
responsible for the formation of the anion in MeCN without the addition of a base is not clear, but this process only happens if oxygen is present in the solution. Although disproportionation is quite common for radicals, it seems quite improbable for galvinoxyl in view of its redox potentials ($E^{\text{red}} = -0.07 \, \text{V}$ and $E^{\text{ox}} = 2.2 \, \text{V vs. SCE}$ in MeCN).\textsuperscript{48} The initially reported unreactivity of galvinoxyl against oxygen\textsuperscript{1} was shown to stem from the inhibition of the oxidation reaction by hydrogalvinoxyl.\textsuperscript{2,49} On the other hand, rapid reduction of galvinoxyl to the galvinoxylate anion in basic media is well documented.\textsuperscript{47} Despite this, it seems justified to consider galvinoxyl to have an extraordinary stability.

Attempts to detect fluorescence from the galvinoxyl radical between 430 and 1100 nm were unsuccessful even in low temperature glasses ($\text{EtOH} : \text{MeOH} = 1 : 1$) and PMMA film. This lack of emission from an upper excited state is consistent with an ultrafast internal conversion to the $D_1$ state. We were not able to look for emission above 1100 nm, but the fluorescence quantum yield and the radiative rate constant of $D_1$ can be expected to be very small owing to its cubic dependence on the transition frequency, and the negligible $D_1 \rightarrow D_0$ transition dipole moment. Inspection of the molecular orbitals shows that the $D_1 \leftarrow D_0$ transition is associated with a charge transfer from the non-bonding oxygen lone pair to the $\pi$-system. This means that in the $D_1$ state, which results from the HOMO $\rightarrow$ HOMO−1 excitation, the unpaired electron is more localized than in the ground state, namely at the oxygen atoms (HOMO−1 in Fig. 2).

Relaxing the geometry in $^2B$ symmetry, i.e. in the symmetry of the $D_1$ excited state, leads to minor structural changes as also concluded from resonance Raman measurements.\textsuperscript{30} According to our calculations, the interplanar angle decreases by $3^\circ$ and the C−O bond elongates by 2 pm, which can be understood by the transfer of an electron from a nonbonding orbital (with the node at the C atom) to the HOMO, which has a node between the C and O atoms (see Fig. 2).

Transient absorption (TA) spectra in various solvents were recorded after $D_9,10 \leftarrow D_0$ excitation of the galvinoxyl radical at 400 nm (Fig. 3A). In all solvents used, the spectra are dominated by a negative band at 430 nm, the bleach signal stemming from the depletion of the ground-state population. This band is as narrow as the steady-state absorption band and does not hint on the presence of stimulated emission from the optically populated state. Additionally, two positive bands contribute to the TA spectra, one that is only present at early pump–probe time delays, and one that grows as time evolves at the expense of the former. Whereas the first TA band is weak and broad and covers essentially the whole observation window, the second one is narrow and located at the red edge.
of the intense bleach band, namely around 440 nm. This latter band decays in parallel to the bleach signal while shifting continuously to the blue. All these transient features decay almost to zero in less than 20 ps. The residual TA spectrum still contains about 5% of the initial bleach and, in MeOH, EtOH and toluene, it exhibits a small positive band with a maximum at 575 nm (better seen in Fig. S1 in the ESI†).

The time evolution of the TA spectra could be well reproduced by target analysis assuming a scheme with three successive first-order steps, \( A_1 \rightarrow A_2 \rightarrow A_3 \rightarrow A_4 \), the resulting evolution-associated difference spectra (EADS) being shown in Fig. 3(B). The shortest time constant, \( \tau_1 \), is close to the IRF of the set-up and the EADS consists of the broad positive band and the strong negative bleach band. The second EADS exhibits only the narrow positive band on the red side of the bleach together with the negative band. However, the amplitude of the bleach band is smaller than in the first EADS, pointing to a partial recovery of the ground-state population in the \( A_1 \rightarrow A_2 \) step. In the third EADS, the positive band peaks at shorter wavelength, whereas the bleach is substantially smaller than in the second EADS, indicating a further recovery of the \( D_0 \) state population. As a consequence, the fastest component with \( \tau_1 \) can be associated with the decay of an electronic excited state to the vibrationally hot electronic ground state, which then undergoes a biphatic vibrational relaxation with \( \tau_2 \) and \( \tau_3 \) to the thermally equilibrated ground state. Since excitation wavelength dependent TA measurements could not be performed owing to the low extinction coefficients of all but the 430 nm band, an identification of the electronic state responsible for the early TA spectra and extinction coefficients of all but the 430 nm band, an identification reflected by \( A_1 \) in Fig. 3 is not possible. From the EADS, it is associated difference spectra (EADS) being shown in Fig. 3(B).

Table 2 Lifetimes extracted from the transient absorption data (IRF 200 fs) in different solvents, and ionization potentials of the solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \tau_1/\text{ps} )</th>
<th>( \tau_2/\text{ps} )</th>
<th>( \tau_3/\text{ps} )</th>
<th>IP_{\text{liq}}^{w}/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>0.18</td>
<td>1.2</td>
<td>5.1</td>
<td>12.2</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.26</td>
<td>1.2</td>
<td>4.1</td>
<td>8.2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.19</td>
<td>1.3</td>
<td>4.6</td>
<td>8.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.21</td>
<td>1.1</td>
<td>6.5</td>
<td>8.6</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.13</td>
<td>1.3</td>
<td>5.9</td>
<td>6.8</td>
</tr>
</tbody>
</table>

* From ref. 56, 59 and 60.

The EADS termed \( A_2 \) and \( A_3 \) show features that are typical of a vibrationally hot ground state, namely an ESA peaking on the red side of the ground-state bleach band and shifting continuously to the blue while decaying. Thus, \( A_2 \) and \( A_3 \) can be viewed as the vibrational hot ground state responsible for the early TA spectra and reflected by \( A_1 \) in Fig. 3 is not possible. From the EADS, it is reasonable to ascribe \( A_1 \) to an electronic excited state but one cannot exclude that the \( D_0 \) state is never populated in the course of the electronic relaxation because of the presence of a conical intersection between higher excited states that could open a more efficient pathway toward \( D_0 \).

The EADS could result from a small coupling between the vibrational modes excited in the internal conversion and the others. On the other hand, the time constant associated with vibrational relaxation, \( \tau_3 \), depends on the solvent and can thus be ascribed to vibrational cooling. However, \( \tau_3 \) does not correlate with solvent properties such as viscosity, dielectric constant, heat capacity or thermal diffusivity. The \( \tau_3 \) values are close to those found with open-shell organic ions,29 and in the range typical for medium sized organic molecules.54

Rapid sample degradation under irradiation with 400 nm pulses at high repetition rate (80 MHz) impeded reliable measurements of the \( D_0 \) state lifetime by fluorescence up-conversion spectroscopy. Since only minor photodegradation was observed in the aforementioned TA measurements (performed at 1 kHz laser repetition rate), the decomposition is most likely related to the excitation of an intermediate with a lifetime between some nanoseconds and microseconds. Indeed, the TA shows a long-lived residual that, in alcohols and tolulene solution, resembles the transient reported by Kuzmin et al. in their flash photolysis experiment upon UV (260–380 nm) excitation.14 Its absorption spectrum peaks at 575 nm (Fig. S1, ESI†), close to the 580 nm absorption maximum reported for the galvinolylate anion. The same band has been detected in pulse radiolysis studies and was also ascribed to the anion.55 We therefore conclude that the species observed in the flash photolysis studies14 is the galvinolylate anion and not the excited state of the galvinolyl radical. In the present case, the galvinolylate anion is most probably formed upon electron capture after multiphotonic ionization of the solvent. Indeed, the TA intensity at 575 nm in MeOH solution scales quadratically with the pump intensity (Fig. S2, ESI†), pointing to a mechanism that includes biphotonic ionization of the solvent at this excitation wavelength and subsequent trapping of the solvated electrons by galvinolyl in accord with the pulse radiolysis studies by Capellos and Allen.55 Such a scheme explains why the highest galvinolylate anion yield is observed in toluene and alcohol solutions, the solvents with the lowest liquid ionization potentials,56 whereas no ionization takes place in MeCN which has a high ionization potential (Table 2).

In view of these results, the appearance of both galvinolyl cation and anion after UV irradiation as reported by Ganyuk et al.15 most probably originates from direct photoionization of the galvinolyl radical, yielding the cation and a solvated electron which is then captured by another galvinolyl to form the anion. Such a mechanism also explains why these authors did not observe the ions upon excitation in the 430 nm band. Considering the extremely short excited-state lifetime of galvinolyl, a bimolecular photoinduced disproportionation reaction as proposed in ref. 13 is unfeasible at moderate concentrations. These authors detected the presence of the cation by its emission and not by absorption, because of its relatively small absorbance. As a consequence, we cannot exclude the formation of the cation in our experiment upon direct multiphotonic ionization of the galvinolyl radical.

The steady-state absorption and emission spectra of the galvinolylate anion in basic ethanol solution are shown in Fig. 4. The presence of fluorescent impurities is responsible for the disagreement between the absorption and fluorescence excitation spectra and leads to a wavelength dependence of the fluorescence properties. According to TA measurements, the \( S_1 \) state lifetime of the galvinolylate anion amounts to
Summary and conclusions

Ultrafast internal conversion from $D_{0,10}$ to $D_0$ was found for the galvinoxyl free radical in all the solvents investigated. The corresponding release of 3 eV electronic energy in less than 200 fs is accomplished by a high density of states, that can be anticipated from the electronic absorption spectrum, and which were reproduced by the DFT calculations. The lowest lying excited state at 0.9 eV is of $\pi$ character but extremely short lived contrary to that of benzyl type radicals, presumably due to the proximity of the ground and possibly of the $D_0$ state. Because of the remarkably high density of states below the optically populated state, the excited molecule benefits from extremely short-lived Franck–Condon factors for non-radiative transitions to lower electronic states and/or does not need to distort much to reach a conical intersection between them. This strongly differs from those molecules with a large energy gap between the electronic states, which need substantial distortion to access a conical intersection to undergo very fast internal conversion.

After this ultrafast internal conversion, the $D_0$ state appears first vibrationally hot and relaxes in a bi-phasic fashion. As has been observed in other cases, the first of the time constants associated with vibrational relaxation is solvent independent. Amounting to 1.2 ps, it is, however, much longer than what might be expected for intramolecular vibrational energy redistribution (IVR) of an organic molecule of this size in liquid solution where IVR time constants of a few tens or hundreds of femtoseconds are typical. The insensitivity to solvent properties also makes an assignment of $\tau_2$ to large amplitude structural changes unlikely.

Our results show that the long-lived transient that had been ascribed to galvinoxyl $D_1$ state is in fact the galvinoxylate anion formed by electron capture after ionization, that can be induced by either UV or intense visible light. Furthermore, contrary to what was proposed in the literature, photoinduced disproportionation of galvinoxyl is a highly improbable process and thus the observed presence of both cation and anion upon UV excitation is due to photoionization.

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References
