Ultrafast photoinduced relaxation dynamics of the indoline dye D149 in organic solvents

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The relaxation dynamics of the indoline dye D149, a well-known sensitizer for photoelectrochemical solar cells, have been extensively characterized in various organic solvents by combining results from ultrafast pump–supercontinuum probe (PSCP) spectroscopy, transient UV-pump VIS-probe spectroscopy, time-correlated single-photon counting (TCSPC) measurements as well as steady-state absorption and fluorescence. In the steady-state spectra, the position of the absorption maximum shows only a weak solvent dependence, whereas the fluorescence Stokes shift $\Delta \nu_F$ correlates with solvent polarity. Photoexcitation at around 480 nm provides access to the $S_1$ state of D149 which exhibits solvation dynamics on characteristic timescales, as monitored by a red-shift of the stimulated emission and spectral development of the excited-state absorption in the transient PSCP spectra. In all cases, the spectral dynamics can be modeled by a global kinetic analysis using a time-dependent $S_1$ spectrum. The lifetime $\tau_1$ of the $S_1$ state roughly correlates with polarity [acetonitrile (280 ps) $<$ acetone (540 ps) $<$ THF (720 ps) $<$ chloroform (800 ps)], yet in alcohols it is much shorter [methanol (99 ps) $<$ ethanol (178 ps) $<$ acetonitrile (280 ps)], suggesting an appreciable influence of hydrogen bonding on the dynamics.

A minor component with a characteristic time constant in the range 19–30 ps, readily observed in the PSCP spectra of D149 in acetonitrile and THF, is likely due to removal of vibrational excess energy from the $S_1$ state by collisions with solvent molecules. Additional weak fluorescence in the range 390–500 nm is observed upon excitation in the $S_0$ state roughly correlates with polarity [acetone (280 ps) $<$ THF (720 ps) $<$ chloroform (800 ps)], yet in alcohols it is much shorter [methanol (99 ps) $<$ ethanol (178 ps) $<$ acetonitrile (280 ps)], suggesting an appreciable influence of hydrogen bonding on the dynamics.

Here we present a comprehensive investigation of D149 in various organic solvents using ultrafast transient absorption spectroscopy, time-correlated single-photon counting (TCSPC) measurements as well as steady-state absorption and fluorescence. The relaxation dynamics of the indoline dye D149, a well-known sensitizer for photoelectrochemical solar cells, have been extensively characterized in various organic solvents by combining results from ultrafast pump–supercontinuum probe (PSCP) spectroscopy, transient UV-pump VIS-probe spectroscopy, time-correlated single-photon counting (TCSPC) measurements as well as steady-state absorption and fluorescence. In the steady-state spectra, the position of the absorption maximum shows only a weak solvent dependence, whereas the fluorescence Stokes shift $\Delta \nu_F$ correlates with solvent polarity. Photoexcitation at around 480 nm provides access to the $S_1$ state of D149 which exhibits solvation dynamics on characteristic timescales, as monitored by a red-shift of the stimulated emission and spectral development of the excited-state absorption in the transient PSCP spectra. In all cases, the spectral dynamics can be modeled by a global kinetic analysis using a time-dependent $S_1$ spectrum. The lifetime $\tau_1$ of the $S_1$ state roughly correlates with polarity [acetonitrile (280 ps) $<$ acetone (540 ps) $<$ THF (720 ps) $<$ chloroform (800 ps)], yet in alcohols it is much shorter [methanol (99 ps) $<$ ethanol (178 ps) $<$ acetonitrile (280 ps)], suggesting an appreciable influence of hydrogen bonding on the dynamics.

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1. Introduction

Indolines have emerged as one of the most frequently used indolines for solar-cell applications is D149, which is depicted in Fig. 1. Surprisingly, so far there has been only very limited information on indoline dynamics after photoexcitation, e.g., a study of Fakis et al. for D149 in toluene and acetonitrile and on Al$_2$O$_3$ and TiO$_2$ surfaces using single-wavelength fluorescence up-conversion, which will be discussed with respect to our current findings below. In addition, DFT/TD-DFT calculations have been reported and assigned considerable charge transfer (CT) character to the $S_1$ state.

Here we present a comprehensive investigation of D149 in various organic solvents using ultrafast transient absorption spectroscopy, time-correlated single-photon counting (TCSPC) measurements as well as steady-state absorption and fluorescence. The relaxation dynamics of the indoline dye D149, a well-known sensitizer for photoelectrochemical solar cells, have been extensively characterized in various organic solvents by combining results from ultrafast pump–supercontinuum probe (PSCP) spectroscopy, transient UV-pump VIS-probe spectroscopy, time-correlated single-photon counting (TCSPC) measurements as well as steady-state absorption and fluorescence. In the steady-state spectra, the position of the absorption maximum shows only a weak solvent dependence, whereas the fluorescence Stokes shift $\Delta \nu_F$ correlates with solvent polarity. Photoexcitation at around 480 nm provides access to the $S_1$ state of D149 which exhibits solvation dynamics on characteristic timescales, as monitored by a red-shift of the stimulated emission and spectral development of the excited-state absorption in the transient PSCP spectra. In all cases, the spectral dynamics can be modeled by a global kinetic analysis using a time-dependent $S_1$ spectrum. The lifetime $\tau_1$ of the $S_1$ state roughly correlates with polarity [acetonitrile (280 ps) $<$ acetone (540 ps) $<$ THF (720 ps) $<$ chloroform (800 ps)], yet in alcohols it is much shorter [methanol (99 ps) $<$ ethanol (178 ps) $<$ acetonitrile (280 ps)], suggesting an appreciable influence of hydrogen bonding on the dynamics.
2.2 UV pump–VIS probe transient absorption spectroscopy

Accuracy 10 fs. The time in the current experiments was 90–100 fs and the time dependence. The pump–probe intensity cross-correlation signals, and can be easily discerned by their characteristic time correlation time were not subtracted from the experiment baseline correction. Solvent signals arising during the cross-pump–probe delay represent the average of three independent element photodiode arrays. Transient spectra for each sample spectra were dispersed by two spectrographs with 512 m beams. Pump and probe pulses were overlapped at magic-angle polarization were collinearly recombined and focused into a quartz flow cuvette containing D149 in the solvent of interest. Transient absorption was detected by an avalanche photodiode using an appropriate set of cut-off filters for the pump beam wavelength. The signal was processed by a lock-in amplifier which used the same 2 MHz reference as the AOM.

2.3 Nanosecond time-correlated single photon counting (TCSPC)

The basic setup of the TCSPC system was described before. In the current measurements, a solution of D149 in THF, acetonitrile or chloroform (OD 0.3) was excited by a pulsed N2 flash lamp (FWHM 2 ns) at a repetition rate of 50 kHz. The unpolarized radiation of the N2 line at 337 nm was selected by a monochromator (Jobin-Yvon H.20 UV, bandwidth: 1–2 nm) and emission was detected at the maximum of the fluorescence spectrum using an identical monochromator combined with a photomultiplier (Philips XP2020). The signal was fed into a time-to-amplitude converter (Tennelec TC 862) connected to a multichannel analyzer (Silena ADC 7423 UHS). A scatter solution (Ludox, Du Pont) and the D149 sample solution were alternately translated into the excitation beam until 1000 counts in the maximum were accumulated. Decay curves were deconvolved with the instrument response function (IRF) resulting in mono-exponential decays. With this setup, single exponential decay time constants down to a few hundred ps can be determined.

2.4 Steady-state absorption and fluorescence

Absorption spectra were recorded on Varian Cary 5E and 5000 spectrometers with baseline correction. Fluorescence spectra were detected using Horiba Jobin-Yvon Fluorolog-3 and Varian Cary Eclipse spectrometers. Fluorescence raw data were corrected for the instrument response function.

2.5 Photostability experiments in the UV

For photostability measurements in the S0 → S1 band of D149 below 400 nm, the light from a cw high-pressure Hg–Xe lamp (Osram HBO, 200 W) was passed through an appropriate set of optical glass filters (Schott UG1 and WG320) and mildly focused into the sample cuvette (10 mm × 10 mm) by a quartz lens (f = 150 mm) at an angle of 90° with respect to the beam path of the absorption spectrometer. The resulting power density at the sample was ca. 50 mW cm⁻².

2.6 Chemicals

The indoline dye D149 was purchased from Inabata UK Ltd. and used without further purification. Solvents had a specified purity of 99% or better. The absorption, fluorescence and TCSPC measurements were carried out at 298 K in nitrogen saturated solution. We note that solutions of D149 in acetonitrile showed absorption shifts in the nm range and sometimes formation of a weak blue shoulder, which are tentatively
assigned to a side-reaction of D149, possibly with O₂ or aggregate formation.

3. Results and discussion
3.1 Steady-state absorption and fluorescence of D149

Steady-state absorption and fluorescence spectra in six organic solvents are depicted in Fig. 2. Characteristic values are summarized in Table 1 including the polarizability $R(n) = (r^2 - 1)/(r^2 + 2)$ and the polarity function $\Delta f = R(\varepsilon) - R(n) = (\varepsilon - 1)/(\varepsilon + 2) - (r^2 - 1)/(r^2 + 2)$, calculated from tabulated $n$ and $\varepsilon$ values.²⁷ The absorption spectra show only a weak solvent dependence. They consist of $D_a$ to the $S_0$ $S_1$ absorption band. They exhibit a weak pedestal in chloroform, which is correlated with solvent polarity ($e.g.$ 2780 cm⁻¹ in chloroform compared to 4050 cm⁻¹ in acetonitrile), indicating that the dipole moment of D149 increases upon photoexcitation, see also Table 1. We note that Fakis et al.¹⁴ reported the fluorescence maximum in acetonitrile at ca. 615 nm, which is blue-shifted by 49 nm with respect to our value. This large difference is likely due to a missing correction of their fluorescence spectrum with respect to detector sensitivity. Similarly, a previous study of Le Bahers et al.¹⁶ reports the $S_1$ emission maximum in methanol at 644 nm compared to the 670 nm found in our study. The difference of 26 nm and the additional shoulder on the red side of their fluorescence spectra also suggest a missing correction for detector sensitivity in that study. A similar explanation might hold for chloroform, where Dentani et al. find the fluorescence maximum at 636 nm,² whereas our value is 643 nm.

Fig. 3(A) contains $S_0 \rightarrow S_0$ steady-state fluorescence spectra of D149 in acetonitrile and THF recorded after $S_0 \rightarrow S_1$ excitation at 487 and 522 nm (dotted lines), respectively, and $S_0 \rightarrow S_2$ excitation at 380 nm (solid lines) for D149 in both solvents. After $S_2$ excitation, we observe a slight red-shift of 130 and 50 cm⁻¹ for the fluorescence in acetonitrile and THF, respectively. Possible reasons for this discrepancy will be discussed in Section 3.4. As can be seen from Fig. 3(B), the fluorescence spectra after $S_2$ excitation show an additional weak pedestal which starts to rise around 26 000 cm⁻¹. It is rather flat and merges with the $S_1$ emission. We note that this result is in contrast to Fakis et al., who observed two distinct emission bands with a dip at ca. 530 nm, which were assigned to separate $S_1$ and $S_2$ emissions.¹⁴ The pedestals in Fig. 3(B) can be assigned to weak $S_2 \rightarrow S_0$ emission, but contributions from an impurity are probably dominant (see Section 3.4). We note that the $S_2 \rightarrow S_0/S_1 \rightarrow S_0$ emission band ratio, which we obtained after deconvolution, is much smaller than in the spectra reported by Fakis et al.,¹⁴ which also suggest a missing correction for detector sensitivity in their experiments. The extremely weak $S_2 \rightarrow S_0$ emission already points toward a very short lifetime of the $S_2$ state. Note also that the $S_2 \rightarrow S_0/S_1 \rightarrow S_0$ emission band ratio in acetonitrile is larger than in THF. We will discuss the resulting implications for the $S_2/S_1$ lifetime ratio in more detail in Section 3.4.

3.2 Transient PSCP spectra and TCSPC experiments

Ultrafast transient broadband absorption spectra $\Delta OD(t)$ of D149 in acetonitrile, methanol and THF are shown in Fig. 4–6, respectively. D149 was excited to the $S_1$ state at 476 nm (acetonitrile), 479 nm (methanol) and 484 nm (THF). Table 2 contains a summary of experimental conditions and kinetic information extracted from the PSCP spectra, including

![Fig. 2](image-url) Absorption spectra (dashed lines) and fluorescence spectra (solid lines) of D149 in different organic solvents. Fluorescence spectra were recorded after excitation at the absorption maximum of the $S_0 \rightarrow S_1$ band in each case.

Table 1 Characteristics of solvent dependent D149 steady-state absorption and fluorescence spectra ($S_0 \rightarrow S_1$ transition)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$R(n)$</th>
<th>$\Delta f$</th>
<th>$\lambda_{\text{Abs, max.}}$/nm</th>
<th>$\rho_{\text{Abs, max.}}$/cm⁻¹</th>
<th>$\lambda_{\text{Fl, max.}}$/nm</th>
<th>$\rho_{\text{Fl, max.}}$/cm⁻¹</th>
<th>$\Delta f_F = (\rho_{\text{Abs, max.}} - \rho_{\text{Fl, max.}})/(\rho_{\text{Abs, max.}}) \cdot 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>0.212</td>
<td>0.711</td>
<td>529</td>
<td>18 920</td>
<td>664</td>
<td>14870</td>
<td>4050</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.203</td>
<td>0.711</td>
<td>528</td>
<td>18 950</td>
<td>670</td>
<td>14690</td>
<td>4260</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.221</td>
<td>0.669</td>
<td>531</td>
<td>18 820</td>
<td>664</td>
<td>14800</td>
<td>4020</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.218</td>
<td>0.651</td>
<td>530</td>
<td>18 870</td>
<td>659</td>
<td>15010</td>
<td>3860</td>
</tr>
<tr>
<td>THF</td>
<td>0.246</td>
<td>0.439</td>
<td>531</td>
<td>18 830</td>
<td>621</td>
<td>15960</td>
<td>2870</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.267</td>
<td>0.293</td>
<td>549</td>
<td>18 230</td>
<td>643</td>
<td>15450</td>
<td>2780</td>
</tr>
</tbody>
</table>

$\Delta f = R(\varepsilon) - R(n)$, where $R(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 2)$ and $R(n) = (n^2 - 1)/(n^2 + 2)$ with the dielectric constant $\varepsilon$ and the index of refraction $n$ of the solvent.
estimated errors from the fitting procedures. A global kinetic analysis will be presented in Section 3.3.

We commence with the PSCP experiments for acetonitrile (Fig. 4): the upper plot shows the early-time dynamics between $0.1$ and $0.22$ ps in steps of $40$ fs. Here, one observes the negative ground state bleach (GSB, $S_0 \rightarrow S_0$) of D149, with a characteristic double peak structure resembling the inverted steady-state absorption spectrum (shown as a dashed blue line in the bottom panel). In addition, nascent stimulated emission (SE) is visible to the red of the GSB, arising from the $S_1$ state prepared by photoexcitation. It is superimposed by weaker structured Raman contributions, which disappear as soon as the pump and probe pulses no longer overlap. Furthermore, there is excited state absorption (ESA) over the whole spectral window. In the GSB region, the superimposed ESA contribution is immediately noticeable from the positive signal at around $430$ nm (probably due to a transition to a higher-lying electronically excited state: $S_1 \rightarrow S_0$). The ESA is much more pronounced to the red ($570$–$770$ nm). In this spectral region, one readily observes the beginning of a spectral development, which is due to solvation dynamics caused by the ultrafast reorientation of acetonitrile molecules, which respond to the altered charge distribution when D149 is excited to $S_1$. This response is reported by the transient red-shift of the SE band of D149.

The solvation dynamics becomes more obvious in the middle panel of Fig. 4, which summarizes the spectral evolution from $0.4$ ps to $1.2$ ps in steps of $40$ fs, and from $1.5$ ps to $3.0$ ps in $500$ fs steps. The SE moves further to the red to approach its equilibrium position (compare the steady-state SE spectrum in the bottom panel), and this process results in a negative signal between $650$ and $770$ nm. At the same time, the superimposed strong $S_1 \rightarrow S_0$ ESA peak centered at ca. $600$ nm band rises further up, due to the disappearing SE in that spectral region. The solvation dynamics in acetonitrile have completely ceased by $3$ ps, which is the expected timescale in this solvent.28

Fig. 3 (A) Steady-state fluorescence spectra of D149 after $S_0 \rightarrow S_1$ (dotted lines) and $S_0 \rightarrow S_2$ (solid lines) excitation for THF (black) and acetonitrile (blue). (B) Magnification of the fluorescence spectra after $S_0 \rightarrow S_2$ excitation shown in (A) in the region where $S_2 \rightarrow S_0$ emission is expected. Spectra in (A) below $11,800$ cm$^{-1}$ have been extrapolated.

The bottom panel shows the final decay of the $S_1 \rightarrow S_0$ ESA bands and the concomitant filling-up of the GSB with a time constant of $t_1 = 280$ ps, which must be dominated by $S_1 \rightarrow S_0$ internal conversion (IC) with a minor contribution of radiative decay. We note that the study of Fakis et al. reported a $S_1$ lifetime of $220$ ps in acetonitrile.14 This is considerably shorter than in our experiments, and is due to the fact that the fluorescence up-conversion transients in that study were measured up to $400$ ps, which is too short to determine an accurate $S_1$ lifetime. In addition to the $S_1$ spectral decay, we see a barely noticeable change in the ESA band structure, with a time constant of $19$ ps. The timescale is consistent with the removal of vibrational excess energy from the $S_1$ state by collisions with solvent molecules,29,30 but $S_1$ structural relaxation could be also responsible for this change.

Inspecting the dynamics of D149 in the other two solvents supports the picture outlined above. For methanol (Fig. 5),
The qualitative development is very similar, yet both solvation and $S_1 \rightarrow S_0$ decay proceed on different timescales compared to acetonitrile. Multieponential solvation dynamics containing fast and slow time constants are found (see the top and middle panels and the global analysis below). Once solvation dynamics has ceased (see the bottom panel which shows clear isosbestic points), the resulting spectrum exhibits SE and ESA band shapes similar to acetonitrile. This is consistent with the comparable Stokes shift of D149 in both solvents, resulting in similar steady-state SE spectra. Interestingly, the lifetime of the $S_1$ state in methanol is much shorter ($\tau_1 = 99$ ps), pointing toward an acceleration of the IC process, as will be discussed below. Concerning the additional 19 ps ESA dynamics in $S_1$ found in acetonitrile, it might be also present in methanol. However, it is difficult to separate it from the slowest component of the methanol solvation dynamics which is 11.9 ps.

The data in THF provide an example for D149 relaxation in a mid-polar solvent with fast solvation dynamics (Fig. 6). Again, an ultrafast transient red-shift of the SE is observed in the top and middle panels (which is completed in less than 10 ps), but the spectral appearance is different from that in acetonitrile and methanol, because the Stokes shift in THF is much smaller. The negative SE signal is therefore located more to the blue (negative peak at 660 nm). As a result, the ESA peak at 596 nm is much smaller than in polar solvents, and another ESA peak is visible further to the red, centered at 726 nm, which is otherwise overwhelmed by the more red-shifted SE in polar solvents. The lifetime of the $S_1$ state is much longer than in acetonitrile and methanol and was independently determined from our TCSPC measurements. A representative trace is shown in Fig. 7, which can be nicely modeled by a clean monoeponential decay with $\tau_1 = 720$ ps. Corresponding TCSPC experiments for D149 in acetonitrile yielded a trace which is slightly wider than the IRF of the TCSPC setup and can be well represented by the decay constant $\tau_1 = 280$ ps from the PSCP experiments. In this case, the time-resolution...
Table 2  Summary of global analysis results for D149 in organic solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>λpump/ nm</th>
<th>τCC/ fs</th>
<th>τ2/ ps</th>
<th>τ1/ ps</th>
<th>τrelax/ ps</th>
<th>τsolv,1/ ps</th>
<th>τsolv,2/ ps</th>
<th>τsolv,3/ ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>476</td>
<td>100</td>
<td>0.4 ± 0.1</td>
<td>280 ± 10</td>
<td>19 ± 10</td>
<td>0.089</td>
<td>0.63</td>
<td>—</td>
</tr>
<tr>
<td>Methanol</td>
<td>479</td>
<td>90</td>
<td>—</td>
<td>99 ± 5</td>
<td>—</td>
<td>0.12</td>
<td>0.99</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>377.5</td>
<td>130</td>
<td>—</td>
<td>0.3 ± 0.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ethanol</td>
<td>377.5</td>
<td>130</td>
<td>—</td>
<td>178 ± 10</td>
<td>—</td>
<td>0.39</td>
<td>5.03</td>
<td>29.6</td>
</tr>
<tr>
<td>Acetone</td>
<td>377.5</td>
<td>130</td>
<td>—</td>
<td>540 ± 20</td>
<td>—</td>
<td>0.187</td>
<td>1.09</td>
<td>—</td>
</tr>
<tr>
<td>THF</td>
<td>484</td>
<td>100</td>
<td>—</td>
<td>720 ± 20</td>
<td>—</td>
<td>0.228</td>
<td>1.52</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>377.5</td>
<td>130</td>
<td>0.6 ± 0.3</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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</table>

*a PSCP experiment: S\(_0\) \rightarrow S\(_1\) excitation at 476–484 nm, UV-pump VIS-probe experiment: S\(_0\) \rightarrow S\(_2\) excitation at 377.5 nm.  
*b Pump-probe cross-correlation of the experiment extracted from the width of the “coherent artifact”.  
*c S\(_2\) and S\(_1\) lifetimes τ\(_2\) and τ\(_1\) from transient absorption experiments. In the case of THF, the S\(_1\) lifetime of 720 ps was extracted from TCSPC experiments. The corresponding TCSPC value for chloroform is (800 ± 20) ps.  
*d Time constant for vibrational relaxation in the S\(_1\) state due to collisions with the solvent (or possibly structural relaxation).  
*e Time constants for solvent relaxation taken from ref. 28 (acetonitrile, ethanol, acetone and THF) and ref. 31 (methanol). Note: τ\(_{solv,1}\) for methanol is for a Gaussian function, whereas in all other cases exponential functions are used.  
*f Time constant cannot be determined, either due to timescale overlap with τ\(_{solv,3}\) (PSCP, methanol) or due to insensitivity of the transients at 755 nm to this process (experiments with single probe wavelength).

of the S\(_1\) state is fairly long compared to collisional relaxation: τ\(_1\) is in the range 99 to 800 ps depending on the solvent, whereas τ\(_{relax}\) is ca. 19–30 ps (estimate based on the values for S\(_1\)).

In the case of THF, the decay S\(_1\) \rightarrow S\(_0\) is fairly slow, and therefore it cannot be covered completely within the time-window of the PSCP experiments. Therefore the S\(_1\) lifetime was determined from our TCSPC experiments and kept constant in the course of the global analysis.

The resulting time-dependent S\(_1\) spectra for D149 in acetonitrile, methanol and THF are shown in Fig. 8. In all cases, the time-dependence is dominated by the transient Stokes shift of the SE. In contrast, the concomitant shift of the ESA peak at around 600 nm is minor suggesting that the energy gap between the S\(_1\) and S\(_0\) states involved in the transition is not changing appreciably in the course of the solvent relaxation. In all cases, the solvation dynamics can be nicely and consistently modeled with the time constants of Horng et al. (acetonitrile, THF)\(^{28}\) and Ernsting and co-workers (methanol),\(^{31}\) for coumarin 153 and rhodamine 110, respectively.

The values are summarized in Table 2: a fast biexponential relaxation in acetonitrile (89 and 630 fs) and THF (228 fs and 1.52 ps) and a more complex response in methanol with one Gaussian and two exponential functions (120 fs, 990 fs and 11.9 ps, respectively). As mentioned above, the additional weak spectral development after completion of the solvent dynamics can be tentatively ascribed to collisional cooling (or possibly also structural relaxation) of the S\(_1\) state, which takes 19 ps in acetonitrile and 30 ps in THF. It might be also present in methanol, however a reliable time constant cannot be extracted due to the overlap with the slowest part of the solvation dynamics.

Fig. 9, examples for kinetic traces of D149 in methanol are shown for selected wavelengths together with fit results (solid black lines) including the contributions from S\(_1\) (green lines) and S\(_0\) (red lines). The traces at 390 and 500 nm show a steep decay (GSB) and a recovery with a time constant of 99 ps (S\(_1\) \rightarrow S\(_0\)), with additional weak curvature in the early part of the transients, which is due to solvation dynamics. At 600 nm, S\(_1\) \rightarrow S\(_0\) ESA is formed, whereas at 720 nm first S\(_1\) \rightarrow S\(_0\) ESA and then S\(_1\) \rightarrow S\(_0\) SE develop. In both cases, the final decay is
also due to the recovery of $S_0$ with a time constant of 99 ps. The superimposed $S_1$ solvation dynamics become particularly clear in the insets of the 600 and 720 nm traces, where the magnification shows the characteristic curvature, which arises from the time-dependent Stokes shift of the SE band.

Additional transient absorption experiments have been performed by employing excitation at 377.5 nm ($S_0 \rightarrow S_2$) and probing in the SE band at 755 nm. These experiments will be discussed in more detail in Section 3.4, but at this point we already mention that the measurements in two additional solvents (acetone and ethanol) can also be nicely described by solvation times from the literature. These values are reported in Table 2 together with the $S_1$ lifetime, which is 178 ps in ethanol and 540 ps in acetone, respectively. Therefore, the lifetime $\tau_1$ of the $S_1$ state approximately correlates with polarity, e.g. acetone ($\tau_1 = 280$ ps) < acetone ($\tau_1 = 540$ ps) < THF ($\tau_1 = 720$ ps) < chloroform ($\tau_1 = 800$ ps). However, interestingly, in protic solvents the lifetime is much shorter [methanol ($\tau_1 = 99$ ps)] < ethanol ($\tau_1 = 178$ ps) < acetone ($\tau_1 = 280$ ps)], suggesting a substantial influence of hydrogen bonding on the dynamics. A similar acceleration of nonradiative processes in alcohols was observed for other molecules, such as 4-aminophthalimide. It is accompanied by an increased Stokes shift in protic solvents, which is also observed for D149 (Table 1).

### 3.4 Lifetime of the $S_2$ state

In addition to the PSCP experiments employing $S_0 \rightarrow S_1$ excitation we have carried out transient absorption measurements with $S_0 \rightarrow S_2$ excitation at 377.5 nm and single wavelength probing at 755 nm, to determine the lifetime of the $S_2$ state. An example for the short-time dynamics in methanol is presented in Fig. 10, which contains the transient absorption signals for $S_1$ excitation (red circles, PSCP) and $S_2$ excitation (black circles) normalized to the same amplitude of the SE (for both transients occurring at ca. 25 ps, not shown here for the sake of clarity). $S_2$ excitation obviously results in additional $S_2 \rightarrow S_n$ ESA, which is responsible for the increased amplitude at early times. The $S_2 \rightarrow S_n$ ESA decays by $S_2 \rightarrow S_1$ IC to form $S_1 \rightarrow S_n$ ESA, which later on becomes dominated by $S_1 \rightarrow S_0$ SE, once solvation dynamics has sufficiently progressed (compare e.g. the 720 nm transient in Fig. 9).

It is obvious that the $S_2$ lifetime has a critical impact on the appearance of the transient, because it influences the width of the peak, its early-time decay, and (to a much smaller extent) also the signal rise. Using the best fit parameters from the PSCP experiments for methanol in Table 2, the $S_2$ lifetime and absorption coefficient were simultaneously varied to obtain an optimized fit, which was reached for $\tau_2 = 0.3$ ps (black solid line in Fig. 10). Contributions of $S_2$ and $S_1$ to the fit are shown as solid blue and solid green lines, respectively. Shorter (longer) lifetimes result in too narrow (broad) simulations, as shown in the figure. Using a similar approach we obtain a lifetime of...
In eqn (1) the $A_F$ denotes the areas of the corresponding fluorescence bands. We obtain the area ratio from the deconvolution of the emission bands in Fig. 3. We note that this deconvolution is not straightforward because the two emission bands overlap. Assuming a simple kinetic scheme involving the nonradiative IC steps $S_2 \rightarrow S_1$ and $S_1 \rightarrow S_0$ as well as the radiative decays from $S_2$ and $S_1$ one arrives at:

$$
\frac{A_F(S_2 \rightarrow S_0)}{A_F(S_1 \rightarrow S_0)} = \frac{\Phi_F(S_2 \rightarrow S_0)}{(1 - \Phi_F(S_2 \rightarrow S_0))\Phi_F(S_1 \rightarrow S_0)}
$$

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Here, $\tau_{rad,i}$ and $\tau_j$ are the radiative and fluorescence lifetimes for the state $i$. We have roughly estimated the radiative lifetime of the $S_2$ and $S_1$ states using the Strickler–Berg formula for the two examples given in Fig. 3. Employing our absorption and fluorescence spectra, an absorption coefficient of 68700 L mol$^{-1}$ cm$^{-1}$ for the maximum of the $S_0 \rightarrow S_1$ band, and wavelength-dependent refractive indices from the literature, we obtain for the $S_1$ state 6.2 ns in acetonitrile and 4.3 ns in THF. The corresponding values for the $S_2$ state are 4.3 ns in acetonitrile and 2.7 ns in THF. With $D_{149}$ in THF, the direct calculation of $\tau_{rad,i}$ from eqn (2) employing the measured $\Phi_F$ (0.140 in nitrogen-saturated THF at 298 K) and $\tau_1 = 720$ ps (Table 2) provides a value of 5.2 ns. This confirms that the Strickler–Berg approach provides a reasonable estimate of $\tau_{rad}$ for $D_{149}$. Using these results and our measured $S_i$ lifetimes $\tau_1 = 280$ and 720 ps in acetonitrile and THF, respectively, we arrive at $\tau_2 = 1.5$ ps in acetonitrile and 3.1 ps in THF. While these time constants suggest a much faster decay of $S_2$ compared to $S_1$, they are still substantially larger than our direct determination of $\tau_2$ from transient absorption spectroscopy. This result means that the observed $S_2$ emission consists in fact mainly of the emission from a small amount of an impurity. This interpretation is also supported by our TCSPC experiments with lamp excitation at 337 nm, where the blue emission band of $D_{149}$ in THF shows a double exponential decay at 460 nm: the first component has a very small time constant (far below TCSPC time resolution), and the second component is very weak (relative amplitude: 1.9 × 10$^{-4}$) and long-lived (decay time constant ca. 20.0 ns). The fast and slow components contribute about 30 and 70% to the overall emission intensity at 460 nm, respectively. The TCSPC experiment is practically not affected by photodecomposition due to the very low excitation power (i.e. photoproducts are not reexcited). This fact allows us to assign the fast component to $S_2$ emission of $D_{149}$ and the long component to the fluorescence of an impurity.

Fig. 10 Comparison of transient absorption profiles of $D_{149}$ in methanol at 755 nm obtained after $S_1$ excitation at 479 nm (PSCP, red circles) and $S_2$ excitation at 377.5 nm (black circles). The black solid line is the best fit for a $S_2$ lifetime of 0.3 ps, with contributions from $S_2$ (blue solid line) and $S_1$ (green solid line). Other black fit lines are from a sensitivity analysis using other $S_2$ lifetimes: 0.2 ps (dash-dotted line), 0.4 ps (dotted line) and 0.6 ps (dashed line). 0.4 ps in acetonitrile and (less accurate due to a worse signal-to-noise ratio) ca. 0.6 ps in THF. Our values are in good agreement with results of Fakis et al., who reported 0.44 ps (toluene) and 0.31 ps (acetonitrile) based on their up-conversion measurements of the $S_2$ fluorescence.14

Our values can be compared with results from another much more approximate indirect approach for obtaining the $S_2$ lifetime by using the area ratio of the $S_2$ and $S_1$ fluorescence bands, which can be estimated from deconvolution of the emission bands in Fig. 3. We note that this deconvolution is not straightforward because the two emission bands overlap. Assuming a simple kinetic scheme involving the nonradiative IC steps $S_2 \rightarrow S_1$ and $S_1 \rightarrow S_0$ as well as the radiative decays from $S_2$ and $S_1$ one arrives at:

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Here, $\tau_{rad,i}$ and $\tau_j$ are the radiative and fluorescence lifetimes for the state $i$. We have roughly estimated the radiative lifetime of the $S_2$ and $S_1$ states using the Strickler–Berg formula for the two examples given in Fig. 3. Employing our absorption and fluorescence spectra, an absorption coefficient of 68700 L mol$^{-1}$ cm$^{-1}$ for the maximum of the $S_0 \rightarrow S_1$ band, and wavelength-dependent refractive indices from the literature, we obtain for the $S_1$ state 6.2 ns in acetonitrile and 4.3 ns in THF. The corresponding values for the $S_2$ state are 4.3 ns in acetonitrile and 2.7 ns in THF. With $D_{149}$ in THF, the direct calculation of $\tau_{rad,i}$ from eqn (2) employing the measured $\Phi_F$ (0.140 in nitrogen-saturated THF at 298 K) and $\tau_1 = 720$ ps (Table 2) provides a value of 5.2 ns. This confirms that the Strickler–Berg approach provides a reasonable estimate of $\tau_{rad}$ for $D_{149}$. Using these results and our measured $S_i$ lifetimes $\tau_1 = 280$ and 720 ps in acetonitrile and THF, respectively, we arrive at $\tau_2 = 1.5$ ps in acetonitrile and 3.1 ps in THF. While these time constants suggest a much faster decay of $S_2$ compared to $S_1$, they are still substantially larger than our direct determination of $\tau_2$ from transient absorption spectroscopy. This result means that the observed $S_2$ emission consists in fact mainly of the emission from a small amount of an impurity. This interpretation is also supported by our TCSPC experiments with lamp excitation at 337 nm, where the blue emission band of $D_{149}$ in THF shows a double exponential decay at 460 nm: the first component has a very small time constant (far below TCSPC time resolution), and the second component is very weak (relative amplitude: 1.9 × 10$^{-4}$) and long-lived (decay time constant ca. 20.0 ns). The fast and slow components contribute about 30 and 70% to the overall emission intensity at 460 nm, respectively. The TCSPC experiment is practically not affected by photodecomposition due to the very low excitation power (i.e. photoproducts are not reexcited). This fact allows us to assign the fast component to $S_2$ emission of $D_{149}$ and the long component to the fluorescence of an impurity.

We also note that our experiments employing $S_2$ excitation suggest the presence of an ultrafast photoinduced process in $D_{149}$, which must proceed either directly from $S_2$ or at high excess energies in $S_1$: for instance, the transient absorption profiles at 755 nm exhibit a small (few percent) residual absorption, which is not present after $S_1$ excitation (not shown here). In the same experiments, prolonged laser excitation in the $S_2$ band at 377.5 nm leads to a change in the steady-state absorption spectrum of the solution, where the $S_0 \rightarrow S_1$ band is asymmetrically broadened (reaches further to the red) by a few nm (the exact value depending on the solvent) and, at the same time, the $S_2$ band reduces in intensity by about 10%. Our reported $S_2$ lifetime therefore possibly contains contributions from $S_2 \rightarrow S_1$ IC and another nonradiative pathway. Interestingly however, the lifetime of the $S_1$ state is independent of excitation wavelength. Indications for the formation of a photoproduct are also obtained in experiments with sub-400 nm excitation in the $S_0 \rightarrow S_2$ band of $D_{149}$ in solution by cw lamp illumination with appropriate filters. In this case, the absorption spectra reach a photostationary state within a few minutes. An example is given in the ESL. Recall also that the $S_1 \rightarrow S_0$ fluorescence band shows a small red-shift when switching from $S_1$ to $S_2$ excitation (Fig. 3(A)). All these observations could be, e.g., tentatively explained by a photoisomerization reaction of $D_{149}$ after $S_2$ excitation, yet a full explanation of this complex behavior certainly requires further experiments, which are beyond the scope of the current paper and are currently ongoing in our laboratories.
4. Conclusions

We have presented a comprehensive study of the photoinduced dynamics of the indoline dye D149 in a range of organic solvents. The dynamics after S1 photoexcitation are fairly simple for such a complex molecule. The increase of the D149 dipole moment upon photoexcitation triggers solvation dynamics on characteristic timescales, which manifest themselves in a transient Stokes shift in the red to near IR region and an accompanying increase of a superimposed prominent ESA band at around 600 nm. The decay of the S1 state proceeds on a timescale between 99 ps (methanol) and 800 ps (chloroform), and is dominated by internal conversion. In protic solvents, the relaxation is considerably faster than in aprotic solvents of similar polarity, suggesting the influence of hydrogen-bonding, which is likely also responsible for the trends in the Stokes shifts. Transient absorption experiments after S2 photoexcitation reveal an ultrafast decay of this state on a sub-picosecond timescale and also the formation of a photoproduct, which will require further characterization.

Regarding the already demonstrated successful application of this dye in photoelectrochemical solar cells the following comments can be made: the S1 lifetime of the “isolated” dye is long enough such that electron injection into semiconductor oxide electrodes (which likely occurs on a 100 fs timescale, possibly with additional picosecond components) should efficiently compete with the intramolecular relaxation of the S1 state of D149, resulting in a high quantum yield for electron injection. The observed generation of a photoproduct after S2 excitation is probably not desirable: it might convert the sensitizer into an inactive form, especially under long-term illumination, but in the most favourable case the photocatalyst (which has a similar spectrum) might inject electrons as well. Such an unwanted side-reaction could however be efficiently suppressed, once the dye is attached to a semiconductor oxide electrode, as has been demonstrated in the case of merocyanine dyes. Investigations along these lines are currently underway in our laboratories.

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Notes and references