Hole injection from P1 dye hot-excited states in p-type dye-sensitized films: a fluorescence study

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Abstract

We present a study of the excited state relaxation dynamics of the photosensitizer P1 used in p-type dye-sensitized solar cells. Comparative femtosecond fluorescence upconversion measurements in solution and in films show that the dye undergoes a picosecond electronic relaxation from the bright Franck–Condon (FC) state to a low-emitting charge-transfer (CT) state in polar environment. The fluorescence is moderately quenched in solution and on the mesoporous Al₂O₃ isolator but dramatically more on NiO semiconductor. We assign this sub-picosecond process to the hole injection thus confirming that the electron transfer is from the FC state directly into the NiO valence band.

Graphic abstract

Keywords Time-resolved fluorescence · Fluorescence upconversion · Excited-state dynamics · Push–pull molecules

Pushing the limits of flash photolysis to unravel the secrets of biological electron and proton transfer—a topical issue in honour of Klaus Brettel.

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1 Introduction

Introduced more than 30 years ago, Dye-Sensitized Solar Cells (DSSCs) is still a research topic that attracts a lot of interest. DSSCs bear the promise of a renewable energy source and even if their performances are largely surpassed by other technologies of solar cells today, the possibility to incorporate all-organic metal-free photosensitizers gives DSSCs a definitive advantage. Still, their performances must be improved and, among the possible directions to go, the

idea of high-efficiency tandem cells is perhaps one of the most exciting [1].

However, the performances of tandem cells are strongly hampered by the poor functioning of the p-type electrode which is still not well understood. Indeed, there are fundamental differences between the functioning of n- and p-type electrodes [2]. In n-type DSSCs, electron injection has been shown to occur over a large time window ranging from the femtosecond to the nanosecond time-scale [3–5], related to fairly high electron injection efficiencies. In p-type DSSCs, on the other hand, the corresponding hole injection seems to occur on a much faster (sub-picosecond) time-scale [6, 7] but the overall photoconversion efficiencies are disappointingly low, probably due to faster recombination processes [8].

For this reason, there is today a large interest to improve the efficiency of p-type DSSCs, but this requires a better picture of which process is failing. Among the reported p-type photosensitizers, the push–pull dye P1 (Scheme 1) is recognized as a standard for p-type DSSCs by many research groups [9]. In spite of its high reputation, the P1 excited state dynamics are far from fully understood. Qin et al. [10] and later Zhang et al. [11] performed both femtosecond transient absorption measurements of P1 in solution and adsorbed on NiO film. In solution, P1 show decay kinetics with a lifetime around 30 ps in acetonitrile, which is unusually fast for normal organic dyes, and 1.3 ns in dibromomethane. Qin et al. made the hypothesis that the fast quenching of the excited state may be due to dye-to-dye electron transfer, but this was contested by Zhang et al. after comparing with the transient spectra obtained by spectroelectrochemistry. On NiO film, the spectral shape was found to correlates well with the sum of the spectrum of the anion $P1^{\bullet-}$ and a broad absorption from 300 nm extending past 1100 nm characteristic of holes in NiO.

In this article, we will provide a set of spectroscopic characterizations of P1, from steady-state spectroscopy to femtosecond fluorescence measurements in solution. Moreover, the hole injection dynamics have been measured in P1-sensitized NiO mesoporous thin film. Our aim is to determine

if the photo-excited dye follows a relaxation path similar to those of other push–pull dyes, that is an intra-molecular charge transfer leading to a new electronic state which is strongly quenched in polar solvents [12–14], if this process also occurs when sensitized on a NiO film and finally if it competes with the hole injection process.

2 Experimental methods

2.1 Chemicals and samples

2.1.1 Chemicals

The dye P1 (full name, 4-(bis-[4-[5-(2,2-dicyano-vinyl)-thiophene2-yl]-phenyl]-amino)-benzoic acid) was provided by Dyenano. The purity of the dye was assessed by HPLC and fluorescence (see Figures S7 and S8). It was then used without further purification. Spectroscopic grade (ACS for spectroscopy) toluene was purchased from Sigma-Aldrich while spectroscopic grade (UVasol) tetrahydrofuran (THF), acetonitrile (ACN) and ethanol (EtOH) were purchased from Merck. All solvents were used without further treatment.

2.1.2 Films

Prior to film deposition, the FTO plates were first cleaned with ethanol and acetone and placed under a UV-Ozone cleaner for 30 min. Al_2O_3 films were prepared as follows. 2.5 g of Al nanoparticles (20% wt in isopropanol, Sigma-Aldrich) were mixed with 10 g of ethyl-cellulose (45 cp in a 80:20 toluene/ethanol solution). 17 g of terpeneol were then added. The mixture was then homogenized by adding 20 mL of pure ethanol using a disperser [ultra-turrax T10 (IKA)] at 5000 rpm. Ethanol and isopropanol were removed using a rotary evaporator. The paste obtained was further homogenized using a grinder until a shiny milky white paste was obtained. The paste was then doctor bladed on a cleaned FTO glass (Solaronix) and heated to 250 °C for 15 min and then at 350 °C for 90 min. The obtained films are white and appear highly scattering. The thickness of the film was about 8 μm as measured with a Stylus Alpha-step profilometer (see Figure S3). NiO films were prepared by doctor blading as described previously [15]. Shortly, a mix of 4.85 g of EtOH and 2.19 g of water is used to dissolve 1.83 g of $NiCl_2 \cdot (H_2O)_6$ and 1 g of pluronic F-127 (Sigma). Viscosity of the mix was assessed to be around 20 cp. Finally, a few drops of the mix are deposited on top of an FTO plate. After a short drying on a 70 °C plate, films are annealed at 400 °C for 30 min. A second layer of film is then deposited. AFM measurements determined the first layer width to be around 350 nm, while the total width of the film was measured close to 0.8 μm (see Figure S3). Both films were sensitized in a

Scheme 1 Structure of dye P1

bath containing P1 (0.020 mM) and chenodesoxycholic acid (CDCA) in a 1:3 ratio diluted in a mixture of DCM and THF (2:1). The co-sensitization of CDCA decreases the dye–dye interaction at the surface of mesoporous film. In our study, we assume that it helps in decreasing the importance of dye–dye relaxation paths. After sensitization, the films are red (Figure S4).

2.2 Spectroscopic measurements

2.2.1 Steady-state spectroscopy

Steady-state absorption spectra were recorded with a Perkin-Elmer Lambda 900 spectrophotometer. Steady-state fluorescence spectra were obtained using an SPEX Fluorolog 3 and corrected for the spectral sensitivity of the detection system. Solutions were placed into 10 mm × 10 mm quartz cells and the absorbance of the samples at the excitation wavelength was kept below 0.05. All experiments were performed at room temperature.

For the representation of fluorescence spectra on an energy scale, they were multiplied by a factor λ^2 [16]. The steady-state Stokes shift ($\Delta\sigma$) was calculated as the difference between the appropriate peak wave numbers obtained from absorption and fluorescence data.

The fluorescence quantum yields (ϕ_f) were calculated from the following equation:

$$\phi_f = \phi_{\text{ref}} \frac{I_f}{I_{\text{ref}}} \frac{1 - 10^{-A_{\text{ref}}}}{1 - 10^{-A}} \frac{n^2}{n_{\text{ref}}^2} \quad (1)$$

where I_f represents the area under the fluorescence spectrum curve, A the absorbance of the solution and n the refractive index of the solution. A solution of Rhodamine 6G in ethanol ($\phi_{\text{ref}} = 0.94$) was used as reference [17]. The part of the fluorescence spectrum outside of our detection range (above 850 nm), was extrapolated using a simplified log–normal function [18].

$$I(x) = I_0 e^{-\rho^2 \left[\ln\left(\frac{x-a}{b}\right) \right]^2} \quad (2)$$

2.2.2 Time-resolved fluorescence in transmission

Time-resolved fluorescence measurements were performed using the fluorescence upconversion (FU) and time-correlated single photon counting (TCSPC) techniques [19]. The excitation source for both experiments was the second harmonic (450 nm) of a mode-locked Ti–Sapphire laser (Coherent MIRA 900) delivering ~ 120 fs pulses with a repetition rate of 76 and 4.75 MHz for FU and TCSPC respectively (in the latter case set by a Coherent 9000 pulse-picker).

For the TCSPC experiments, a Becker & Hickl GmbH SP-630 PC card was used [20]. The fluorescence from a standard quartz cell was collected and focused onto the entrance slit of a small monochromator (Jobin–Yvon HR250), equipped with a photomultiplier detector (Hamamatsu R1564U). The instrumental response function was about 50 ps, as measured with the main Raman line in water.

For the FU measurements in solution, a home-built setup in transmission mode, already described in detail elsewhere [18] was used. In this setup, a 1.0 mm-type I BBO sum-frequency crystal was used for mixing the fluorescence and the fundamental laser pulse, providing an instrumental response function of about 350 fs (full width at half maximum, fwhm). We judge that the time resolution of our transmission FU setup is better than 200 fs after deconvolution, depending on the signal-to-noise ratio [21]. For excitation, we used an average excitation power at 450 nm of about 10 mW. The spectral correction of the detection line was obtained by recording the fluorescence spectra of two reference compounds (Coumarin-153 in EtOH and RK1 in THF) [5, 22] 200 ps after excitation, where all spectral relaxation is finished, and scaling them to the corresponding corrected steady-state fluorescence spectra. The time-resolved experiments (FU and TCSPC) were performed at magic angle.

2.2.3 Front-face fluorescence upconversion

Due to the films being opaque and/or scattering, the FU setup above could not be used and was adapted to work in a front-face geometry as already described previously [5]. Briefly, the pump beam (15 mW, 200 fs, 4 mm), travelling slightly out of plan, is focused on the film by a lens ($f = 150$ mm). The fluorescence is collected and focused by a pair of 1-inch silver parabolic mirror ($f = 10$ cm) with a small incident angle ($\sim 2^\circ$) on a BBO crystal (Castech, 3 mm). The fundamental is removed using a filter (Schott WG475, 3 mm). The probe (800 mW, 200 fs) is focalized and overlapped on the BBO crystal to obtain the upconversion gating effect. The sum is collimated and send to a low-noise PM detector (Hamamatsu, R1527P) coupled to a monochromator (Jobin–Yvon, Horiba Gemini 180) with a spectral resolution set to 4 nm. To limit photo- and thermal degradation, the sample is rotated and translated in the plan perpendicular to the pump propagation. After optimization of the planarity, the time resolution, as measured by the third harmonic generation in the aforementioned BBO crystal, was comparable (300 fs fwhm) to that obtained in transmission mode. However, the instrument response function of our FU measurements on films was found to increase (fwhm ≈ 500 fs), probably due to sample roughness and excitation penetration depth.

2.2.4 TRFS fitting

The mean position of the fluorescence $\sigma(t)$ was extracted from the time-resolved fluorescence spectra by fitting each individual spectrum with a log-normal function (Eq. 2). Using the independent parameters obtained from these fits, σ was calculated as:

$$\sigma(t) = a(t) + b(t)e^{(3/4\beta(t)^2)}. \quad (3)$$

The total intensity I_f was obtained by numerically integrating each recorded spectrum in the energy representation.

The time-dependencies of σ and I_f were fitted in a second stage. The time-dependent mean position $\sigma(t)$ was fitted using a bi or tri-exponential model:

$$\sigma(t) = \sigma_\infty + \Delta\sigma_d \cdot C(t) = \sigma_\infty + \Delta\sigma_d \cdot \sum_{i=1}^{n=3} a_i e^{-t/\tau_i}. \quad (4)$$

The dynamic Stokes shift, $\Delta\sigma_d$, was measured as the difference between the maximal mean position and the asymptotic value of the mean position. The time-dependent total fluorescence intensity $I_f(t)$ was fitted following a multi-exponential model with up to four exponentials where the largest characteristic times was fixed to the characteristic time obtained by TCSPC measurements.

$$I_f(t) = \text{irf} \otimes I_0 \cdot \sum_{i=1}^{n=4} a_i \cdot e^{-t/\tau_i}. \quad (5)$$

The injection characteristic time was obtained by fitting the total fluorescence with a stretched exponential function providing a mean decay time $\langle\tau\rangle$ using the following equations:

$$I(t) = \text{irf} \otimes I_0 \exp(-t/\tau)^\beta. \quad (6)$$

$$\langle\tau\rangle = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right). \quad (7)$$

In Eq. 7, Γ is the gamma function. The injection time τ_{inj} and the injection efficiency η_{inj} were then calculated using the mean decay times of P1 when sensitized on Al_2O_3 and NiO [32]:

$$\tau_{\text{inj}} = \frac{\langle\tau_{\text{Al}_2\text{O}_3}\rangle \langle\tau_{\text{NiO}}\rangle}{\langle\tau_{\text{Al}_2\text{O}_3}\rangle - \langle\tau_{\text{NiO}}\rangle}. \quad (8)$$

$$\eta_{\text{inj}} = 1 - \frac{\langle\tau_{\text{NiO}}\rangle}{\langle\tau_{\text{Al}_2\text{O}_3}\rangle}. \quad (9)$$

3 Results

3.1 P1 in solution

3.1.1 Steady-state spectroscopy

The normalized steady-state absorption and fluorescence spectra of P1 in the four different solvents used in the present study (toluene, THF, EtOH and ACN) are shown in Fig. 1. For clarity, all the spectra are shown on a wavenumber scale.

The absorption spectra are constituted of two bands, a first strong one around 500 nm/20,000 cm^{-1} and a second, weaker one around 350 nm/28,000 cm^{-1} . Interestingly, the first band is significantly red-shifted in EtOH, perhaps due to the protic character of this solvent. Moreover, the first band also shows a more or less pronounced “shoulder” on the high-energy side, indicating the presence of several electronic transitions. Referring to calculations, the first band can be considered as a superposition of the transitions HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO + 1 (B3LYP/6-31G (d)) [10]. The HOMO is delocalized over the whole molecule, including the carboxyl attachment group, while the LUMO is more localized on the acceptor part. This gives a clear CT character to the first absorption band, which evidently is interesting for its use as photosensitizer.

Fig. 1 Normalized steady-state absorption and fluorescence spectra of P1 in toluene (black), THF (red), EtOH (blue) and ACN (green). The absorption spectra were normalized at the peak of the lowest energy band. The fluorescence spectra (symbols) were excited at 500 nm and interpolated using a lognormal function (solid line)

Table 1 Spectroscopic parameters of P1

Solvent	$\epsilon(20\text{ }^{\circ}\text{C})$	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{fluo}}^{\text{a}}(\text{nm})$	$\Delta\sigma(\times 10^{-3}\text{ cm}^{-1})$	$\phi_f(\times 10^2)^{\text{a}}$	$\tau_{\text{F}}(\text{ns})^{\text{b}}$
Toluene	2.4	486	554	2.6	8.8 ± 0.2	0.40 ± 0.01
THF	7.6	486	630	5.8	46 ± 1	< 0.02 (0.7) 1.54 ± 0.02 (0.3)
EtOH	25.1	502	688	5.7	0.4 ± 0.2	< 0.02 (0.99) 2.55 ± 0.08 (0.01)
ACN	38.8	480	704	6.8	0.2 ± 0.1	< 0.02 (0.97) 0.60 ± 0.01 (0.03)

^aExcitation wavelength: 500 nm^bExcitation wavelength 450 nm, probed at 550 nm, the relative amplitudes are given in parentheses

The fluorescence spectra are built up of one single band, but they are significantly more sensitive to the solvent polarity than the absorption spectra. In non-polar toluene, the relatively narrow spectrum peaks around 550 nm and can be seen to be weakly structured (vibronic structure). In slightly more polar THF, the spectrum broadens and shifts about 80 nm to the red. In the polar solvents ACN and EtOH, the fluorescence spectra broaden even more and shift beyond 700 nm.

The spectral shifts increase thus drastically with the solvent polarity, as shown by the Stokes shift, which increases from about 2600 cm^{-1} in toluene to about 6000 cm^{-1} in the more polar solvents (Table 1). The change in fluorescence quantum yield with solvent polarity is even more drastic (Table 1), decreasing from 0.46 in THF to 0.2–0.4 in ACN and EtOH. Interestingly, the quantum yield in non-polar toluene is only 0.09, indicating that the excited state relaxation processes cannot be ascribed to only the solvent polarity—other effects are also involved.

3.1.2 Time-resolved spectroscopy

3.1.2.1 Time-resolved fluorescence decays, TCSPC and FU The fluorescence decays at 550 and 700 nm of P1 in toluene, THF, EtOH and ACN were measured by TCSPC (Figure S1), providing the lifetimes reported in Table 1. As can be seen, the fluorescence lifetimes of P1 vary enormously between “non-polar” and “polar” solvents. This is very much in line with the findings from steady-state spectroscopy. At both fluorescence wavelengths, the decays are largely mono-exponential on the sub-ns to ns time-scale with lifetimes that range from 1.7 ns in THF to limited by the setup time resolution ($< 20\text{ ps}$) in EtOH and ACN. We attributed the long-lived fluorescence component detected in ACN and EtOH to an impurity (Figure S8) due to its low amplitude.

Surprisingly, the lifetime in non-polar toluene is much shorter than that obtained in THF. Since the fluorescent state is much more stabilized in THF ($\lambda_{\text{F}} = 630\text{ nm}$) than in toluene ($\lambda_{\text{F}} = 554\text{ nm}$), this is in contradiction with a simple

Fig. 2 Fluorescence decays (squares) measured by FU and fits (solid lines) of P1 in **a** toluene, **b** THF, **c** ACN and **d** EtOH at 550 nm (blue) and 700 nm (red) after excitation at 450 nm

non-radiative deactivation scheme governed solely by the energy-gap law. This will be discussed in more details below.

For this reason, the early-time evolution of the fluorescence was studied in the four solvents toluene, THF, ACN and EtOH using FU. The corresponding kinetics are shown in Fig. 2.

The early time-evolution of the P1 fluorescence shows a rather complex behavior. In the three more polar solvents, a rapid sub-picosecond/picosecond decay is observed at shorter wavelengths with a corresponding rise at longer

wavelengths-independent. We remark that this is not the case in toluene for the simple reason that the steady-state fluorescence is significantly blue-shifted in apolar solvents. This first phase is followed by a slower decay with a wavelength independent lifetime in accordance with the TCSPC measurements.

The fitted time-constants for the picosecond decay and rise are very close indicating that they may share a common origin. Such a behavior may be explained by a rapid spectral shift associated with the solvation process or an energy transfer between two states. However, single-wavelength data do not allow discriminating between the two possibilities. To do this, time-resolved fluorescence spectra (TRFS) are needed.

3.1.2.2 Time-resolved fluorescence spectra The time-resolved fluorescence spectra (TRFS) of P1 in the four solvents toluene, THF, ACN and EtOH are shown in Fig. 3.

An intriguing aspect of the TRF spectra shown in Fig. 3 is that, at comparable concentrations, the intensity of the signal in ACN is weaker compared to those in the three other solvents (toluene, THF and EtOH). This could be due to

aggregation, as already suggested by Qin et al. [10]. However, we believe that the origin of the remaining FU signal is of monomeric origin, since only strongly allowed transitions are detected by this technique.

From this figure it is also clear that the solvent influences strongly, not only the fluorescence intensity, but also the spectral dynamics. These dynamics are visibly not mono-exponential; instead “fast” and “slow” phases can be discerned. Except for toluene where the fluorescence intensity increases, a fast picosecond spectral relaxation accompanied by an equally rapid drop in fluorescence intensity can be observed. This quenching is more intense in ACN (~80%) than in THF or in EtOH (~40%). In all solvents however, this first phase is followed by a seemingly mono-exponential fluorescence decay.

However, it is difficult, and may be misleading, to compare the behaviors in different solvents without performing a stricter analysis.

To this purpose the TRFS were treated in the same manner as the steady-state fluorescence spectra. Briefly, the spectra were first represented on an energy scale by multiplying by a factor λ^2 and then, each individual time-resolved

Fig. 3 Contour plots of time-resolved fluorescence spectra (TRFS) of P1 in **a** toluene, **b** THF, **c** ACN and **d** EtOH after excitation at 450 nm

Fig. 4 Time-evolution of the total fluorescence intensity $I_f(t)$ (black dots) and the fitted curves (solid black line) and the mean position of the emission $\sigma(t)$ (red circles) and the fitted curves (solid red lines) for P1 after excitation at 450 nm in **a** toluene, **b** THF, **c** ACN and **d** EtOH

spectrum was fitted separately by a log-normal model function. The spectrally integrated intensity $I_f(t)$ and the spectral position $\sigma(t)$ (the mean frequency of the emission band) are extracted from the fitting procedure uncorrelated which allows independent analyses of the two observables. The temporal evolutions $\sigma(t)$ and $I_f(t)$ for P1 in the four solvents are shown in Fig. 4. These data were finally fitted using multi-exponential model functions and the fitted parameters are given in Table 2.

Except for toluene, both the spectral relaxation $\sigma(t)$ and the integrated intensity $I_f(t)$ display bi-phasic behavior with

a fast sub-pico- to picosecond component and a much slower one, ranging from several to tens of picoseconds.

The total amplitude of the dynamic Stokes shift increases drastically with solvent polarity; from only 1000 cm^{-1} in toluene to more than 5000 cm^{-1} in ACN. Indeed, half or more of the spectral relaxation occurs within a picosecond in all four solvents. Then, the rest of the spectral relaxation takes place with a characteristic time varying from solvent to solvent: 3.0 ps in THF, 4.1 ps in toluene, 6.7 ps in ACN and finally, 20 ps in EtOH. In EtOH, the spectral shift seems

Table 2 Characteristic times (τ_i , in ps) and associated amplitudes (in parentheses) obtained for the adjustment of the total fluorescence intensity $I_f(t)$ and of the mean position of the emission band $\sigma(t)$ of P1 in toluene, THF, EtOH and ACN and sensitized on Al_2O_3 and NiO

	$I_f(t)$			$\sigma(t)$		σ_∞	$\Delta\sigma_d$
	τ_1	τ_2	τ_3	τ_1	τ_2		
<i>Toluene</i>	/	/	300	0.4 (0.51)	4.1 (0.49)	17 170	1000
<i>THF</i>	1.6 (0.44)	15.0 (0.24)	1500 (0.32)	0.6 (0.60)	3.0 (0.40)	15 710	2270
<i>EtOH</i>	1.2 (0.31)	10.1 (0.36)	60 (0.33)	0.8 (0.50)	20 (0.50)	14 830	3000
<i>ACN</i>	0.4 (0.61)	3.7 (0.14)	38 (0.25)	0.4 (0.93)	6.7 (0.07)	13 350	5140
<i>Al₂O₃</i>	0.8 (0.65)	8.0 (0.21)	83 (0.14)	0.9 (0.54)	18 (0.46)	15 550	1460
<i>NiO</i>	< irf (0.79)	2.2 (0.21)	/	1.8	/	14 410	2210

to continue beyond the point where the intensity has reached the zero level.

The characteristic lifetime of the integrated intensity, on the other hand, decreases with solvent polarity. In polar ACN, $I_f(t)$ and $\sigma(t)$ are perfectly superimposable during the first picoseconds, before the slower second phase begins. In THF and EtOH, the two curves are quite similar, but with the fluorescence quenching being somewhat slower than the spectral relaxation. A marked difference is the very different behavior of $I_f(t)$ and $\sigma(t)$ in non-polar toluene. In this solvent, $I_f(t)$ shows a weak picosecond rise while $\sigma(t)$ red-shifts rapidly. In all four solvents, the second phase consists only of a slower fluorescence quenching with a lifetime similar to that measured by TCSPC.

The observed spectral dynamics in polar solvents are reminiscent of polar solvation dynamics which have been examined thoroughly in the past, notably by Maroncelli et al. [23, 24]. To better judge to what extent the dynamic Stokes shifts of P1 are due to solvation dynamics, the curves for P1 were compared with the “neat” solvation dynamics measured in the same solvents using the “inert” probe molecule C153. To this end, the time-constants for the time dynamic Stokes shifts were fixed to the values reported in the literature and $\sigma(t)$ curves were reconstructed for the four solvents, only adjusting the amplitude of the spectral shift. Resulting curves are shown in Figure S2.

As can be seen in this figure, the spectral dynamics observed for P1 in toluene are perfectly well described by the three-exponential solvation dynamics reported in the literature for C153. It can thus be concluded that the relaxation of P1 in toluene is solely governed by the solvation dynamics since the presence of additional (inter- or intra-molecular) processes would likely slow down the spectral relaxation. It is interesting to note that the total Stokes shift is also comparable for the two molecules (930 and 1000 cm^{-1} for C153 and P1 in toluene, respectively). In this context, the total absence of any ultrafast fluorescence quenching for P1 in toluene unequivocally shows that the dye molecule does not undergo an electronic relaxation in toluene.

In the more polar solvents, the correlation between reconstructed and observed curves is not good indicating the existence of other excited state relaxation processes, a slower and more complex solvation dynamics for P1 or a combination of both. To quantify the amount of discrepancy, an additional free-floating exponential term was added, which results in a much better accordance between reconstructed and observed $\sigma(t)$ curves. A visual comparison is shown in Figure S2 and the parameters obtained in Table S1. In THF and in ACN, the observed spectral relaxation dynamics are slower than the expected solvation dynamics. This is in line with the added time-constants, 5.9 and 1.5 picoseconds respectively, which are much longer than the reported solvation dynamics. In EtOH, on the other hand, the observed relaxation

dynamics is faster than the reported solvation dynamics. Accordingly, the additional picosecond time-constant represents an intermediate value, 1.1 picoseconds, much faster than the slower 5 and 30 ps time-constants normally attributed to the protic character of the solvent. This may seem surprising, but we note that the mismatch is apparent only during the first few picoseconds. At longer times, the slower relaxation of P1 in EtOH is conform to that of C153, i.e. solvation dynamics. Interestingly, the additional time-constants needed for P1 in ACN (1.5 ps) and in EtOH (1.1 ps) are very close, making it tempting to assume a common origin.

To resume, in polar solvents, an additional picosecond term appears in the spectral dynamics which could be attributed to more complex solvation dynamics or the presence of other relaxation processes in the excited state.

3.2 P1 in film

3.2.1 Steady-state spectroscopy

To obtain the steady-state absorption and fluorescence spectra of monomeric (exempt of self-interactions) P1 on NiO and Al_2O_3 films they were co-sensitized with CDCA. Absorption spectra of both films are similar (Figure S4) although their optical densities are different due to the properties and thickness of the oxide. Their fluorescence spectra present similar maxima (14,700 cm^{-1} (680 nm) for Al_2O_3 and 15,000 cm^{-1} (667 nm) for NiO. However, the fluorescence of the P1-sensitized NiO film is about ten times weaker than that of the corresponding Al_2O_3 (see Figure S5).

3.2.2 Time-resolved spectroscopy

3.2.2.1 Time-resolved fluorescence decays The fluorescence decays of the P1-sensitized Al_2O_3 and NiO films were measured by FU after excitation at 450 nm. Representative decays at several wavelengths are shown in Figure S6. For both films, it is clear that the fluorescence decays are multi-exponential and strongly wavelength-dependent.

On Al_2O_3 , the fluorescence shows a bi-exponential behavior at shorter wavelengths consisting of a rapid first phase (up to 10 ps) followed by a slower decay. This behavior gradually disappears in favor of a purely mono-exponential behavior at longer wavelengths. The longer time-constant is about 80 ps at all wavelengths > 600 nm.

On NiO, the fluorescence quenching is much faster (< 10 ps) at all wavelengths. The decays are characterized by a sub-picosecond component whose amplitude is greater for shorter wavelengths. The longer time constant is as fast as 3 ps at all wavelengths > 600 nm, which is significantly faster than in the case of Al_2O_3 .

In line with the observations in solution, the wavelength dependence may be interpreted as being caused by a spectral

Fig. 5 Contour plot of of time-resolved fluorescence spectra (TRFS) of P1 co-adsorbed on **a** Al_2O_3 and **b** NiO after excitation at 450 nm

Fig. 6 Temporal evolutions of the total fluorescence intensity $I_f(t)$ (black squares) and the mean position of the emission band $\sigma(t)$ (red circles) of P1 co-adsorbed on **a** Al_2O_3 and **b** NiO . The corresponding

multi-exponential fits are shown by solid lines. The excitation wavelength was 450 nm

relaxation taking place on a sub picosecond to-picosecond time-scale as seen for the dye in solution. However, for neither of the two films, no “rise” in fluorescence intensity is observed at longer wavelengths, which would definitely confirm the occurrence of a spectral relaxation.

3.2.2.2 Time-resolved fluorescence spectra The time-resolved fluorescence spectra of the P1-sensitized mesoporous films of Al_2O_3 and NiO are shown in Fig. 5. In both cases, the spectral shift is relatively small (20–30 nm) compared to what was observed in solution-phase. It is apparent that the total fluorescence quenching is very efficient and occurs on a pico to-sub-picosecond time-scale which is consistent with what was observed for the single-wavelength fluorescence decays.

The time evolutions of the band position and the total intensity obtained by the lognormal fitting were then interpolated using multi-exponential fits as shown in Fig. 6. All the fitted parameters are given in Table 2.

The longer component of the fluorescence of P1-sensitized films is shorter than in solution. On Al_2O_3 , the slowest component is nearly four times faster than in toluene, while on NiO , the lifetime is even shorter than in ACN and the emission has completely vanished within 10 ps. For comparison, the average lifetimes $\langle\tau\rangle$ are 0.6 ps on NiO and 20 ps on Al_2O_3 .

On the contrary, the spectral relaxation is slower. On Al_2O_3 it is not finished after 60 ps when the low intensity makes it difficult to follow beyond this point within the sensitivity of our measurements. On NiO the situation is even

less clear as the fluorescence is totally quenched before the spectral relaxation can occur. While the spectral relaxation dynamics are bi-phasic on Al_2O_3 , it is well-described by a mono-exponential function on NiO, probably due to the very limited time window. The total Stokes shifts $\Delta\sigma_d$ are larger than in toluene but two or three times lower than those measured in ACN. This is rather due to a lower value of $\sigma(t=0)$ compared to that obtained in solution than to the final value of σ_∞ . This may be partly due to the limited time resolution of our reflection measurements which could lead to an underestimation of any sub-picosecond spectral relaxation.

Comparing the time-dependencies of the spectral relaxation and the total fluorescence intensity (Fig. 6) separately for Al_2O_3 , and NiO is very instructive. On Al_2O_3 the two curves are perfectly overlapping during the first 10 ps (Fig. 6a), while on NiO, the two curves diverge from the beginning, the fluorescence quenching being much faster than the spectral relaxation.

We also notice an unusual phenomenon in the time-evolution of $\sigma(t)$ at short times. The fluorescence band first shifts toward the blue by a few hundred cm^{-1} before the “normal” red-shift sets in. We rule out the possibility of an experimental error because the same behavior was observed for FU measurements performed in transmission geometry. A possible explanation is that it is due to a transient Stark effect created by the charge separation due to the injection [25]. Interestingly, the σ_∞ values of the P1-sensitized films are comparable those obtained for P1 in polar solvents such as EtOH ($14,830\text{ cm}^{-1}$) or THF ($15,710\text{ cm}^{-1}$).

4 Discussion

The experimental results presented above allow us to make some direct comparisons of the excited state behavior of the dye P1 in solution and in films when sensitized on an insulator (Al_2O_3) and on a hole-acceptor semiconductor (NiO).

4.1 The excited state relaxation dynamics in solution

The relaxation dynamics in the excited state for the dye P1 can be decomposed into two phases. The first phase, from 0.1 to around 10 ps, corresponds to the relaxation of the vertically excited Franck–Condon state and is solvent dependant. The second phase rather appears to be a simple decay back to the ground state.

In toluene, the dynamic Stokes shift is relatively small (1000 cm^{-1}) compared to the more polar solvents (Table 2). The time-evolution of this spectral relaxation is very similar to the “pure” solvation dynamics (Figure S2) and takes place with the two time-constants 0.4 and 4.1 picoseconds. Furthermore, striking is the total absence of any picosecond

fluorescence quenching. One may thus assume that P1 only undergoes a rather weak solvation in toluene during the first phase; indicating a low or no CT character for the relaxed S1 state. Later on, the total intensity decays mono-exponentially with a time-constant of about 300 picoseconds. Interestingly, this value is significantly shorter than what is predicted by the Strickler–Berg equation ($\tau_{\text{rad,SB}} = 1.7\text{ ns}$, see the SI).

In the more polar solvents, THF, EtOH and ACN, the total fluorescence intensity is quenched by more than 50% (70% in ACN) (Fig. 4) after only 10 ps. In parallel, the spectral relaxation occurs faster than the fluorescence quenching but slower than the “true” solvation dynamics (Table S1). The total Stokes shift in THF is more than twice that in toluene but remains still moderate (2270 cm^{-1}) compared to the more polar solvents like ACN (5140 cm^{-1}). In the second phase, the fluorescence decays mono-exponentially with a lifetime of the relaxed excited state varying between 1.5 ns in THF and 38 ps in ACN.

We also note that, in EtOH, the spectral dynamics are more complex, being “faster” than solvation dynamics measured with C153 during the first picoseconds before evolving more slowly than the other solvents at longer times, in accordance with the literature.

4.2 The radiative character of the relaxed excited state in solution

As described above, in polar solvents, the total fluorescence intensity of P1 is very rapidly but partially quenched on a time-scale of a few picoseconds. This partial quenching of the fluorescence may be explained by the following:

1. a system with two initially coexisting excited populations, both of which decay toward the ground state—or a dark state—but at different rates. In this case, the quenching is explained by a *partial population decay*.
2. an excited state (S_1) undergoing an electronic relaxation toward a less bright excited state, leading to a decrease in the radiative rate constant k_{rad} . In this case, the quenching is caused by a *decrease of the emission transition dipole moment*.

However, the transfer from a high-energy level to a low-energy level is clearly seen in the TRFS. In other terms: the lower state is indirectly populated which contradicts the two-population hypothesis.

The values of k_{rad} and $k_{\text{nr,rad}}$ (calculated from the fluorescence lifetime τ_f and the fluorescence quantum yield ϕ_f) for the four solvents studied are given in Table 3. As can be seen, both values change dramatically going from non-polar toluene to polar EtOH and ACN. This can be taken as a strong evidence for a change in the electronic nature of the

Table 3 Radiative and non-radiative rate constants (in ns⁻¹) and radiative lifetimes (intrinsic lifetime of the fluorescent state in the absence of non-radiative relaxation, in ns) for dye P1 in the four studied solvents

	$k_{\text{rad}}(\text{ns}^{-1})$	$k_{\text{nr}}(\text{ns}^{-1})$	$\tau_{\text{rad}}(\text{ns})$	$\tau_{\text{rad,SB}}(\text{ns})$
<i>Toluene</i>	0.21	2.1	4.8	/
<i>THF</i>	0.27	0.32	3.7	1.7
<i>ACN</i>	0.053	26	17	/
<i>EtOH</i>	0.067	17	15	/

emitting state when going from non-polar to more polar solvents. The radiative rate constants k_{rad} are similar in toluene and THF on one hand, and in ACN and EtOH on the other. The non-radiative rate constants k_{nr} in toluene and THF are fairly low but much higher for ACN and EtOH.

We therefore assume the existence of two excited electronic states, the directly excited state, labeled S_1/FC , and a state with significantly higher charge-transfer character labeled S_1/CT . While the S_1/FC is the lowest excited state in the vertical absorption transition for all solvents, the relative position of the relaxed S_1/CT state depends strongly on the solvent polarity. Only in the more polar solvents is the S_1/CT state sufficiently stabilized to open the path for an electronic $S_1/\text{FC} \rightarrow S_1/\text{CT}$ relaxation. For example, in toluene, the S_1/CT state is not stabilized, so S_1/FC remains the upper state in both absorption and emission. In ACN and EtOH, on the other hand, the S_1/CT state is strongly stabilized and becomes the upper state in emission.

However, the behavior of P1 in THF does not really fit into this simple scenario. The relatively large Stokes shift and the very fast (2–15 picosecond) fluorescence quenching are not compatible with a single S_1/FC state undergoing only solvation dynamics. Moreover, the non-radiative rate constant is significantly smaller than that measured in toluene. On the other hand, the observations in THF cannot be ascribed to an electronic $S_1/\text{FC} \rightarrow S_1/\text{CT}$ relaxation, as outlined above. The radiative rate constant radiative is too high to correspond to a CT state. But the most intriguing observation is the surprisingly long fluorescence lifetime (1.5 ns), five times longer than in toluene. A possible explanation could be the existence of one, or several, intermediate state(s) between S_1/FC and S_1/CT as already assumed for similar dyes [26]. As shown in Fig. 7, we propose an energy diagram for P1 in the four solvents summarizing our interpretation of the observations.

4.3 The excited state relaxation dynamics in films

The behavior of P1 when grafted on Al_2O_3 is extremely similar to the behavior of the dye in a polar solvent. Of course, the partial fluorescence quenching could be attributed to dye–dye interaction on the surface. However, we

Fig. 7 Energy diagram of the different states involved in the relaxation of P1 in solution. The relaxation process involves several excited states of more or less pronounced CT character with an accessibility governed by the solvent polarity

assume that it is not the case for two reasons. Firstly, P1 was co-sensitized with CDCA to limit such interaction. Second, the TRFS are well adjusted by a single log–normal function at every moment of the spectral relaxation. Therefore, we assume that P1 undergoes an electronic relaxation to a less radiative S_1/CT when grafted on Al_2O_3 in the first picoseconds following excitation. The latter has a lifetime of about 80 ps, which is comparable to the 38 ps in ACN and 60 ps in EtOH.

On NiO, on the contrary (Fig. 6b), the fluorescence quenching of dye P1 is much faster (0.6 ps) than the spectral relaxation (1.8 ps). Thus, the fluorescence quenching does not seem to be linked to the relaxation of the dye but rather to another non-radiative process. The marked difference between the fluorescence quenching dynamics for the P1-sensitized insulator Al_2O_3 and the semiconductor NiO leads us to assign this non-radiative relaxation pathway to the hole injection into NiO.

4.4 Injection quantum yields

The relaxation dynamics in general and the hole injection in particular are complex processes. Therefore, describing the time-evolution of the total fluorescence intensity using a multi-exponential approach (Eq. 5) does not automatically quantify the injection process. Instead, we used a hybrid model function (Eq. 6), including a stretched exponential to extract the mean characteristic time $\langle\tau\rangle$ with which the characteristic time and the efficiency of injection can be calculated (Eq. 8 and 9).

For the P1 dye, the NiO injection efficiency is very high (97%) due to the extremely fast hole injection (0.6 ps). The P1/NiO system had already been measured by TAS by Qin et al. [10] and by Zhang et al. [11] and the characteristic

injection time was estimated to 200 fs with slower components in the range of 1–20 ps. However, those values were obtained without comparison with the dynamics on Al_2O_3 . Moreover, in the study by Qin et al., the sensitized NiO film was immersed in an ACN solution containing Li^+ ions which are capable of modifying the relative position of the valence band and thus the injection dynamics. In our case, the films are co-sensitized by CDCA to reduce intermolecular interactions, known to quench the fluorescence. Finally, the injection time obtained may be overestimated due to the instrument response function of our FU measurements on films (fwhm $\approx$ 500 fs).

As quenching is faster than spectral relaxation on NiO and by assuming that the electronic relaxation to S_1/CT takes place with similar time-constants on NiO as on Al_2O_3 , it implies that the hole injection is much faster than the electronic relaxation. In other words, the hole injection from P1 into NiO takes place nearly instantaneously from the S_1/FC state.

On the other hand, the spectral relaxation of P1 on NiO, with a characteristic time-constant of 1.8 ps, may still be, at least partially, related to the hole injection as the higher energy population may be more likely to be involved in the injection process. This phenomenon can be described as a “boiling-off” process where the “hotter” levels inject faster than the lower ones and was already discussed in our previous work involving n-type DSSC RK1/TiO_2 [5]. We concluded for that system that injection was maybe not as fast as previously thought and that new dyes for n-type cells should be designed taking into consideration the relaxed electronically excited structure. Studying P1 on thin NiO film under air with our methodology, we do not reach the same conclusion for p-type cells as the injection is faster. The same experiments but with complete cells should be performed to reach a definitive conclusion.

4.5 Comparing with the literature

To our knowledge, there are two previous studies of the excited state dynamics of P1 in ACN solution and on NiO film, both performed by femtosecond transient absorption spectroscopy [10, 11].

In ACN solution, Qin et al. [10] observed a strong transient absorption band around 600 nm characterized by a fast bi-exponential (0.36 ps/2.8 ps) rise accompanied by an equally fast apparent red-shift. The band then decays with a time-constant of 32 ps. They assigned this band to radical cation/anion species formed by an intermolecular electron transfer following aggregation in ACN. They did not specifically consider the possibility of solvation dynamics but in their Fig. 9 a negative band that may be the stimulated emission can be seen to shift rapidly from about 725 nm toward longer wavelengths. We remark that this SE band is probably

further red-shifted by the overlapping with the strong TA band around 600 nm. Zhang et al. [11] agreed with the results of Qin et al. but did not attribute the fast (34 ps) decay to intermolecular electron transfer, as the transient spectra did not correspond to those obtained by spectroelectrochemistry. They also performed additional measurements in dibromomethane, where they observed a small red-shift followed by a long-lived (1.3 ns) excited state lifetime.

On NiO film, Qin et al. observed an even faster 0.23 ps rise of the transient absorption around 610 nm and they assign this ultrafast process to electron injection. The signal then decays in a multiscale manner (2.7 ps, 17 ps, 205 ps). A slower red-shift of the signal was ascribed to solvation dynamics (on the NiO film). This is very surprising since the solvent induced stabilization of a low-lying excited state is in general stronger than that of a higher excited state, leading to a blue-shift of the corresponding transient absorption band. In the study by Zhang et al. a multi-exponential fit at a single wavelength (480 nm, corresponding to the bleach of P1) yielded three characteristic times of 0.17, 1.3 and 20 ps which were all attributed to the injection process. They also performed additional measurements on a P1-sensitized NiO film prepared with the air-stable solid electron conductor, phenyl-C61-butyric acid methyl ester (PCBM), in which case they observed similar injection dynamics as for P1 on NiO.

While TRF, and in particular FU, only monitors strongly allowed transitions from the excited state populations (i.e. emission from “bright” states) TA probes in principle all excited state populations, including those of non-emitting states (i.e. “dark” states) as long as an optical transition toward a higher excited state is possible.

Comparing our findings with those reported in the literature, we are inclined to believe that the sub-ps to-ps dynamics observed by FU in ACN solution are rather due to solvation dynamics (< 1 ps) and the formation of the CT state (3.7 ps in our study and 2.8 ps in theirs). We do not exclude the possibility of aggregation (dimers in particular for a carboxylic acid in ACN), but the fluorescence detected by FU at short times corresponds to a strongly allowed transition, probably of monomeric origin. The fast fluorescence quenching, which corresponds to the formation of the CT state (3.7 ps) is close to the fast rise observed in TAS (2.8 ps). The subsequent decay of both the FU and TA signals are very similar (38 ps in their study and 32 ps in ours), proving that they have a common origin. The results of Zhang et al. obtained in dibromomethane ($\epsilon = 7.7$ at 10 °C) are similar to what we observed in THF: a limited red-shift is followed by a long-lived excited state.

Regarding the P1-sensitized NiO film, FU shows a rapid quenching (bi-exponential with the two time-constants < 300 fs and 2.2 ps or stretched with an “average” time-constant of 0.6 ps) assigned to the hole injection. This

is in good accordance with the 0.23 ps rise and subsequent 2.7 ps decay observed by TA and attributed to the hole injection by Qin et al. as well as the faster components (0.2 and 1.3 ps) measured by Zhang et al.. However, our FU experiments could not detect the presence of a slower ~ 20 ps component in the injection. We acknowledge that the sensibility of our setup might not be enough to detect a low amplitude (22% according to Zhang et al.) slower decay. Especially if the decaying specie is not very radiative like the relaxed excited state of P1, which is populated in with an average time of 9 ps according to our measurements on Al_2O_3 . In conclusion, by comparing our results with the literature, we do not disregard the possibility of a second relaxation process, where the dye undergoes a spectral relaxation prior to injection; but our results suggest that it is not the main relaxation path.

4.6 A comparison with other injection rate measurements

It is worthwhile to compare our results on P1 with injection kinetics reported in the literature. In the case of p-type cells, no FU measurements have been reported to this date, making it difficult to make a direct comparison with our results. On the other hand, a handful of studies using TAS have been published. It is worth noting that very similar injection times (5.9 and 7.4 ps respectively) were obtained for C255-sensitized TiO_2 films (n-type) when examined by both FU and TAS [27]. Based on this observation we think that it is worthwhile to compare with the TAS measurements on dye-sensitized NiO solar cells. Apart from the already mentioned report of a 0.23 ps hole injection in a P1-sensitized NiO cell [10], another TPA-based dye with two bodipy acceptor groups also revealed very fast kinetics, about 1 ps [28, 29]. With a covalently linked peryleneimide–naphthalenediimide dyad as sensitizer, hole injection into NiO was observed to take place with average time-constant of approximately 0.5 ps [30, 31].

It is difficult to draw any general conclusion about charge carrier injection dynamics in p-type cells from only these reports, but what is striking is that the injection times are all very fast, less or equal than 1 ps. This is significantly faster than the injection times reported for n-type sensitized TiO_2 films. The reported electron injection times τ_{inj} span a relatively wide range, from about 1 ps to more than 10 ps, depending on the specific dye and the electrolyte used.

For example, the two D- π -A n-type dyes TH305 [32] and TPC1 [33], which have similar structures to P1 with an identical triphenylamino (TPA) donor group but different acceptor groups, the injection times measured by FU were 1.5 and 16 ps respectively.

In another study, the same coumarin dye (C343) was used as a photosensitizer for both n- and p-type systems. Using FU, Giannouli et al. reported 7 and 77 ps injection times on TiO_2 and ZnO respectively [34], while Morandeira et al. [6] reported an injection time of only 0.2 ps on NiO in a TAS study.

In this context, it is worth noting that two TAS studies of n-type model solar cells using TPA-based D- π -A dyes [35, 36] gave significantly faster electron injection times than FU studies of other n-type model solar cells [31, 32].

5 Conclusion

This work is based on the acquisition and treatment of time-resolved fluorescence spectra of the push–pull molecule P1. It is indeed crucial to handle full spectra, and not single-wavelength decays, to disentangle the total intensity variations from the spectral dynamics. This is compulsory to discriminate intra-molecular processes (such as population changes and/or variations of the transition moment caused by charge transfer) from intermolecular interactions, in particular solvation dynamics. The present work also highlights the advantage to compare time-resolved fluorescence spectra obtained both in solution and in solid phase.

In solution, the excited state relaxation of P1 is very reminiscent to that of other push–pull dyes despite structural differences. In particular, the relaxation dynamics depend strongly on the solvent polarity. In non-polar toluene, the dynamics are determined by the solvation dynamics and no electronic relaxation occurs. Even though the CT character is enforced in the relaxed excited state.

In the more polar solvents, the situation is quite different. The fast partial quenching of the total fluorescence intensity shows that P1 undergoes an electronic relaxation in the excited state ($S_1/\text{FC} \rightarrow S_1/\text{CT}$). The dynamics of this change of state are determined by the solvation dynamics resulting in a complex spectral relaxation. The solvent therefore plays a dual role, energetic and dynamic, because the polarity of the medium changes the relative order of the excited states.

On films, the excited state relaxation of P1 is more complex. The analysis of the fluorescence dynamics of P1-sensitized Al_2O_3 lead us to believe that a similar electronic relaxation ($S_1/\text{FC} \rightarrow S_1/\text{CT}$) is responsible for a partial quenching of the fluorescence on film. The relaxed excited state then decays in about 80 ps. On the semiconductor NiO, the fluorescence quenching is dominated by an extraordinary rapid phase, which is faster than the spectral relaxation. Therefore, we conclude that injection occurs from the directly excited S_1/FC state before the electronic relaxation occurs. From our point of view, reproducing these observations in full working cells (and not with sensitized thin film) could definitely

validate that injection is an efficient process for p-type solar cells.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

Ethical approval Not applicable.

Data availability All data reported in the Figures and the Tables can be obtained from the authors upon request.

Code availability An executable version of the home-made fitting program used can be obtained from the authors upon request. All the Origin 8.1SR2 scripts used in data treatment (log-normal fitting of the TRFS) are available upon request.

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