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# Inclusion of *Push-Pull* N-Methylpyridinium Salts within Surfactant Hydrogels: Is Their Excited State Intramolecular Charge Transfer Mediated by Twisting?

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In order to get a deep insight into the environment-dependent photophysics of *push-pull* pyridinium derivatives, two N-methyl-pyridinium salts were dissolved within surfactants hydrogels. Surfactant viscoelastic solutions can potentially block or at least limit the torsion of these fluorescent dyes, uncovering the nature of the excited states involved in their deactivation. The excited state dynamics of the two molecules in hydrogels was investigated by means of femtosecond transient absorption spectroscopy, revealing the distribution of the dyes between the hydrophobic domains and the water pools making up the microscopic structure of the surfactant hydrogels. The comparison between the spectral shapes of those transients experiencing an aqueous surrounding and those embedded in the hydrophobic domains allowed the fully relaxed excited state to be assigned to a twisted intramolecular charge transfer (TICT) state. The latter cannot be formed in the rigid hydrogel domains where the excited state charge separation is thus prevented and the stationary fluorescence comes from a scarcely polar locally excited (LE) state.

## Introduction

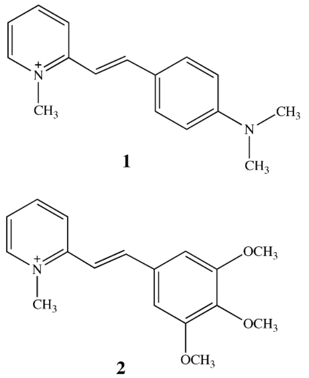
The derivatives of (aminostyryl)pyridinium are widely used as fluorescent dyes, in that their multi-fluorescent behavior is particularly sensitive to the immediate environment they can experience.[1-8] Due to their *push-pull* character, these compounds can undergo significant photoinduced charge transfer, which makes them suitable for many applications, such as non-linear optical (NLO) materials,[9,10] biological markers[11] and fluorescence indicators for neurons,[12,13] to name but a few.

In some recent works of ours,[14-16] considerable attention was devoted to the rich excited state dynamics of a well-known N-methylpyridinium salt, DASPMI (compound **1** in Chart 1). The role of intramolecular charge transfer (ICT) in its deactivation has been controversially discussed, in that solvation and ICT processes, often occurring in the same time scale, are difficult to disentangle and may be confused. In fact, through femtosecond transient absorption measurements carried out in a large series of solvents, we found out two different behaviours for DASPMI depending on the polarity of the medium: fast solvation leading to an ICT state occurs in polar solvents, whereas an intermediate transient characterized by a lifetime significantly longer than solvent relaxation is detected in low polar media.[14] Thanks to the employment of the powerful fluorescence up-conversion technique combined with the shrewd TRANES (time-resolved area normalized emission spectra) analysis, we settled the debate on the widely speculated existence, even in the highly polar aqueous solutions, of an intermediate emissive state: a scarcely polar locally excited (LE) state, populated upon excitation from the polar ground state. The LE then gives an intramolecular charge transfer (ICT) state through back charge shift to the donor moiety, that is the N,N-dimethylamino-phenyl substituent, with the ICT process being as fast as solvation in polar solvents.[16] One challenging question, which still needs to be examined in depth, is whether the steady-state fluorescence of this and analogous molecules occurs from a planar (P) or twisted (T) ICT state.

Quantum-mechanical calculations corroborated this latter hypothesis, at least in polar solvents.[14,16,17] The investigation of the conformational equilibrium in the ground state, evaluated by comparison of the formation enthalpies, revealed the presence of one major stable conformer for the molecule under investigation.[14] This conformer has a planar structure which is slightly affected by the excitation to the LE state. A twisting occurring along with the charge transfer process and favoring the charge separation has been recently calculated through high-level vibronic computations based on density functional potential energy surfaces, revealing the presence of two emissive minima in the excited state of DASPMI.[16] Specifically, it has been reported that the transition from the LE to the TICT minimum involves the twisting of the N-methylpyridinium group around the quasi-single bond with the ethene bridge.[16]

This twisting motion is expected to greatly stabilize the excited state of DASPMI, whose recovery to the ground state would therefore be extremely fast as a result of efficient internal conversion.[14] This explanation fits well the fast solvation-controlled deactivations of the dimethyl-amino derivative in water, whose longest-living transient is defined by a time constant of about 5 ps and whose fluorescence quantum yield is extremely low (about $10^{-3}$).[14]

In order to try and address the critical issue regarding the nature of the emitting excited states also from an experimental point of view, viscosity- and temperature-dependent studies have already been performed, revealing a multi-fluorescent behavior which may be adequately described by invoking a twisted ICT state.[18-20] In particular, our group carried out some measurements on DASPMI in methanol/glycerol mixtures.[14] The choice was driven by the similar dielectric constants of the two solvents, which make it possible to be almost independent of polarity effects and only subjected to changes induced by increasing viscosity. The decay constant of the ICT state in methanol/glycerol (50:50, v/v) was found to be four times the lifetime of the same component in pure methanol because of the alleged TICT nature of the relaxed $S_1$ state. However, some doubts persist and a direct experimental proof still misses.

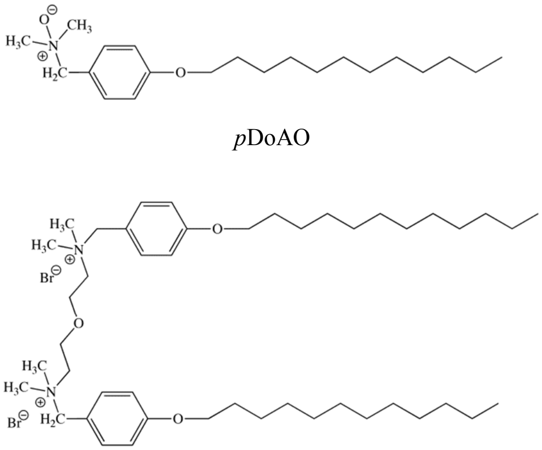


1

2

**Chart 1.** Molecular structures of the *trans* (E) isomers of the iodides of 2-D-ethenyl-1-methylpyridinium. D = 4-(dimethylamino)phenyl (**1**) and 3,4,5-trimethoxyphenyl (**2**).

A step forward in this sense could be taken by resorting to surfactant hydrogels of intertwined wormlike micelles,[21-23] used to entrap the molecule. Two surfactants were chosen for this purpose: the zwitterionic *p*DoAO and its di-cationic *Gemini* counterpart (Chart 2), whose hydrogels, offering an extremely rigid matrix, can potentially block the excited state twisting of DASPMI. The molecular structure of the single chain and *Gemini* surfactants forming the viscoelastic solutions comprises one or two aromatic rings respectively.[24,25] This feature may favor the interaction with the *push-pull* compound by π-π stacking, in spite of the electrostatic repulsion between the positive charge of the methylpyridinium ring and the likewise positive charge localized on the surfactant head group. The *p*DoAO and *Gemini* hydrogels, formed from aqueous solutions of the two surfactants in deionized water, have also been previously morphologically characterized by means of SEM measurements,[23] which revealed a porous surface super-arrangement of interconnected lamellae and a non-uniform distribution of pores with an average diameter of some micrometres.



*p*DoAO

*Gemini*

**Chart 2.** Structures of *p*-dodecyloxybenzyldimethylamine oxide (*p*DoAO) and bis-[2-(N,N-dimethyl-N-p-dodecyloxybenzylammonium bromide)-ethyl]-ether (*Gemini*).

Moreover, the role played by the charge shifts was investigated by expanding the study to a second molecule belonging to the family (compound **2** in Chart 1), differing from DASPMI in the donor moiety (3,4,5-trimethoxy-phenyl substituent) and characterized by a reduced electron-donor strength.[14,15]

In this paper, we try to provide compelling arguments to cast some light on the excited state dynamics of the two molecules, unravelling the nature of the diverse excited states involved in the deactivation of these extensively studied fluorescent dyes.

## Results and discussion

The two molecules were dispersed in the viscoelastic micellar solutions of the two surfactants, where they were studied in terms of spectral and photophysical properties (Table 1) and excited state dynamics (Table 2). Interestingly, with respect to what observed in water, the absorption properties are not affected by the presence of the gel matrix while the fluorescence maximum undergoes an atypical hypsochromic shift (Figure 1 and 2), which is quite unexpected considering the negative solvatochromism of the absorption band and fluorescence invariance upon increasing solvent polarity peculiar to these molecules in homogeneous solution. Fluorescence quantum yields increase by a factor 5 and one order of magnitude for **1** in *p*DoAO gel and *Gemini* gel, respectively, while the emission intensity of **2** enhances by nearly 70% in both hydrogels, irrespective of the surfactant structure. Apparently, the association of the two compounds within the hydrophobic domains provided by the intertwined wormlike micelles is not complete, since the gel matrix does not alter the overall photophysics of the methyl-pyridinium salts to a great extent. However, the remarkable shift in the fluorescence spectrum and the non-negligible increase of $\phi_F$ are clear signs of at least a partial permeation.

**Table 1.** Spectral properties and fluorescence quantum yields of compounds **1** and **2** in water (W), *p*DoAO hydrogel and *Gemini* hydrogel.

| | ***1*** | | | | ***2*** | | | |
|---|---|---|---|---|---|---|---|---|
| ***Medium*** | $\lambda_{abs}$/nm | $\lambda_{em}$/nm | $\Delta\nu$/cm$^{-1}$ | $\phi_F$ | $\lambda_{abs}$/nm | $\lambda_{em}$/nm | $\Delta\nu$/cm$^{-1}$ | $\phi_F$ |
| W$^a$ | 438 | 589 | 5850 | 0.001 | 353 | 546 | 10010 | 0.003 |
| *p*DoAO gel | 437 | 568 | 5280 | 0.005 | 354 | 532 | 9380 | 0.005 |
| *Gemini* gel | 437 | 565 | 5180 | 0.01 | 354 | 540 | 9730 | 0.005 |

$^a$Data retrieved from reference 14.

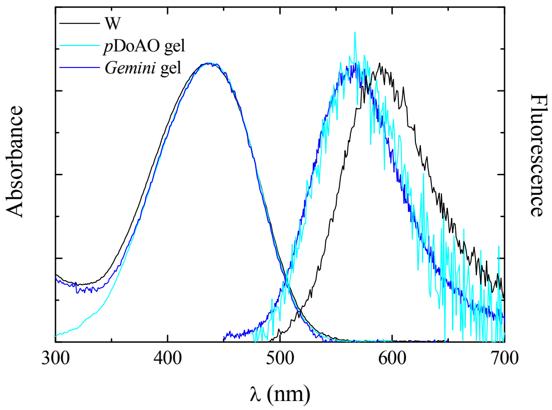


**Figure 1.** Normalized absorption and emission spectra of **1** in W, in *p*DoAO and *Gemini* hydrogels.

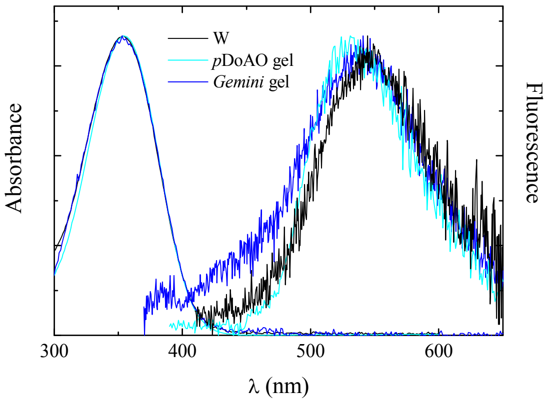


**Figure 2.** Normalized absorption and emission spectra of **2** in W, in *p*DoAO and *Gemini* hydrogels.

**Table 2.** Excited state spectral and kinetic properties of compound **1** and **2** in W, *p*DoAO hydrogel and *Gemini* hydrogel obtained by femtosecond transient absorption spectroscopy ($\lambda_{exc}$ = 400 nm).$^a$

| | ***1*** | | ***2*** | | |
|---|---|---|---|---|---|
| ***Medium*** | *λ/nm* | *τ/ps* | *λ/nm* | *τ/ps* | ***Assignment*** |
| W$^b$ | | | 535(–) | 0.24 | Solv.$_i$ |
| | **570(–)** | **0.70** | **550(–)** | **0.91** | **Solv.$_d$/S$_1$(LE)*** |
| | **520(+), 610(–)** | **4.4** | **<510(+), 580(–)** | **25** | **S$_1$(TICT)*** |
| *p*DoAO gel | | | 505(–), 590(+), 630(+) | 0.20 | Solv.$_i$ |
| | **570(–)** | **0.34** | **<490(+), 540(–)** | **1.0** | **Solv.$_d$/S$_1$(LE)* W** |
| | **520(+), 610(–)** | **5.6** | **<505(+), 580(–)** | **27** | **S$_1$(TICT)* W** |
| | **575(–)** | **150** | **<495(+), 545(–)** | **190** | **S$_1$(LE)* Gel** |
| | | | **585(–)** | **rest** | **S$_1$(TICT)* Gel** |
| *Gemini* gel | | | 550(+) | 0.28 | Solv.$_i$ |
| | **560(–)** | **0.70** | **<485(+), 530(–)** | **1.2** | **Solv.$_d$/S$_1$(LE)* W** |
| | **520(+), 610(–)** | **5.8** | **<505(+), 575(–)** | **28** | **S$_1$(TICT)* W** |
| | **565(–)** | **210** | **525(–)** | **590** | **S$_1$(LE)* Gel** |

$^a$Spectral properties refer to the Species Associated Spectra (SAS) calculated by Target Analysis. The symbols (+) and (–) stand for positive and negative signals, respectively.

$^b$Data retrieved from reference 14.

In order to rationalize the uncommon behavior of the emission of **1** and **2**, femtosecond transient absorption measurements were carried out on both hydrogels, achieving impressive results (shown in Figures 3-5 and summarized in Table 2 along with data previously collected in pure water, here reported for comparison purposes). The biphasic nano-environment provided by the hydrogels needs to be taken into account for a thorough understanding of the experimental data.[26] Hydrogels are made up of aqueous pools filling the voids left by the micellar entanglements, so that the solute molecule can be partitioned between the more hydrophobic gel phase and the hydrophilic water phase.[24,27,28] Since N-methylpyridinium salts show pseudo-amphiphilic features, having a polar cationic portion and a hydrophobic aromatic moiety, their distribution between the two domains can be envisaged. The excited state deactivation proved therefore straightforward. For either molecules in both hydrogels, the same transients revealed in water in terms of identical spectral and kinetics features are detected in the biphasic environment (cf. Table 2 and Figure 3-5), pointing out a major distribution in the aqueous pools. They can be assigned to the LE and ICT states, the former evolving in the same time-scale of the solvation and thus mixed with its contribution.[14,16] Nevertheless, the presence of at least one longer-living transient associated to those molecules embedded in the micellar supramolecular aggregates is needed to aptly fit the experimental data. This signal was found to be more significant for **1** rather than for **2**, probably because of the bulkier trimethoxy-phenyl substituent of the latter compound when compared with the dimethylamino-phenyl of **1**. Its greater hindrance supposedly limits the permeation of **2** within the nano-scaled gel matrix. The transient associated to the confined molecules is indeed characterized by a time constant much longer than those detected in water, but the most relevant piece of information comes from its spectral shape, for it closely matches the features of one of the transients experiencing an aqueous surrounding (panel C, Figure 4 and 5). More precisely, the stimulated emission signal of the gel-permeating molecules resembles that of the water solvation component behind which the contribution of a LE state is masked. It means that the excited molecules in the gel phase are confined in their LE state which is thus not able to convert into the energetically stabilized ICT state. The non-planarity of the latter could hence be inferred: the viscoelastic gel blocks the molecule impairing the charge separation by hindering the twisting around the quasi-single bond. This conclusion can be drawn in light of the tremendous viscosity of the surfactant hydrogels, even when compared with methanol/glycerol mixtures where the excited state charge transfer process was previously found to still take place.[14]

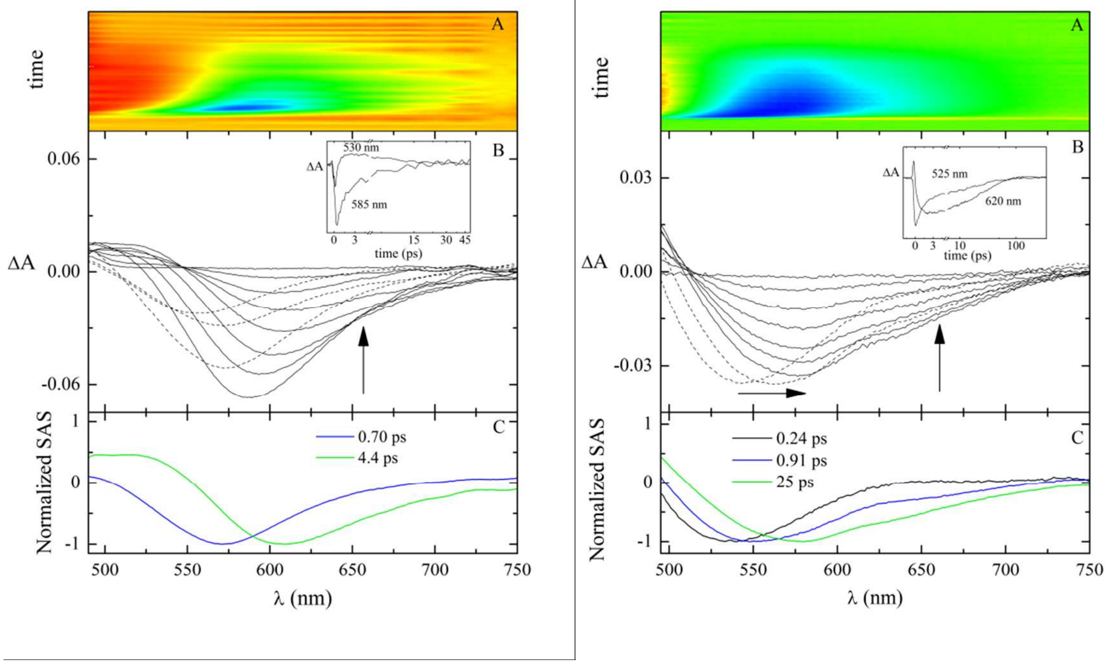


**Figure 3.** Pump-probe absorption spectroscopy of **1** (left graph) and **2** (right graph) in W ($\lambda_{exc}$ = 400 nm):[14] (A) contour plot of the experimental data, (B) time-resolved absorption spectra (the first in dashed lines) recorded at increasing delays after the laser pulse (inset: decay kinetics at meaningful wavelengths, with a linear scale for the first picoseconds and a *log* scale for longer times), and (C) Normalized Species Associated Spectra (SAS) calculated by Target Analysis.

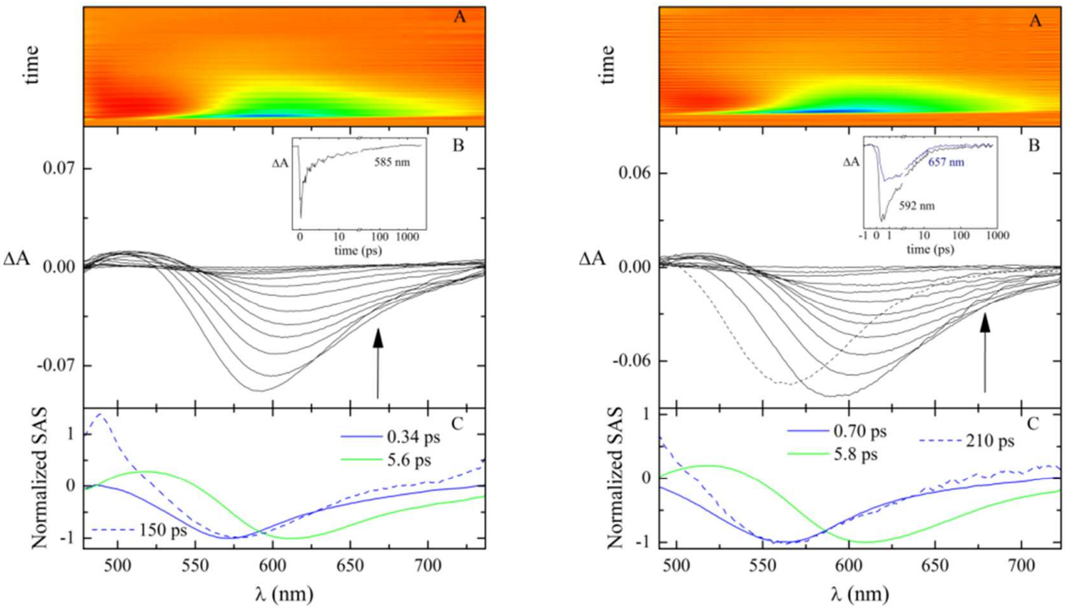


**Figure 4.** Pump-probe absorption spectroscopy of **1** in *p*DoAO hydrogel (left graph) and *Gemini* hydrogel (right graph) ($\lambda_{exc}$ = 400 nm): (A) contour plot of the experimental data, (B) time-resolved absorption spectra (the first in dashed lines) recorded at increasing delays after the laser pulse (inset: decay kinetics at meaningful wavelengths, with a linear scale for the first picoseconds and a *log* scale for longer times), and (C) Normalized Species Associated Spectra (SAS) calculated by Target Analysis.

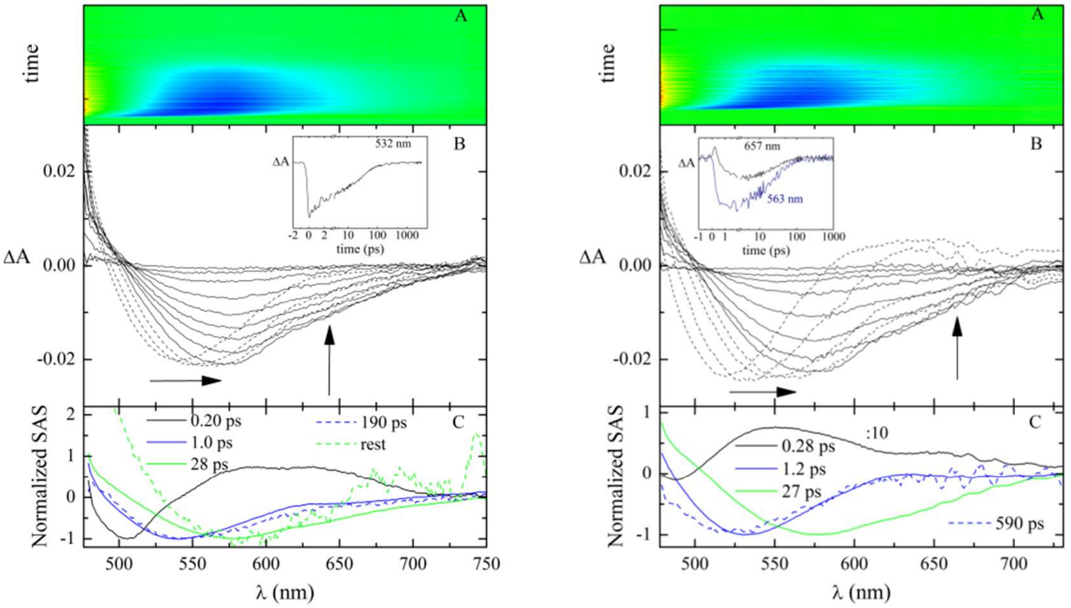


**Figure 5.** Pump-probe absorption spectroscopy of **2** in *p*DoAO hydrogel (left graph) and *Gemini* hydrogel (right graph) ($\lambda_{exc}$ = 400 nm): (A) contour plot of the experimental data, (B) time-resolved absorption spectra (the first in dashed lines) recorded at increasing delays after the laser pulse (inset: decay kinetics at meaningful wavelengths, with a linear scale for the first picoseconds and a *log* scale for longer times), and (C) Normalized Species Associated Spectra (SAS) calculated by Target Analysis.

As additional confirmation of the long-debated twisted character of the ICT state, the excited state dynamics of **2** in *p*DoAO gel shows an extremely weak signal which was fitted with a further component (*rest*, see Table 2) whose decay outlasts the time window of the Excited State Absorption (ESA) experiment (3200 ps). Its spectral shape is once again revealing in that it matches the Species Associated Spectrum of the molecules in the TICT state detected in water (panel C, Figures 3 and 5) and hence attributed to the TICT state reached in the gel phase. This transient was never observed for **1** nor evidence of its occurrence was detected for **2** in *Gemini* gel. In fact, being the electron-donor character higher for the dimethylamino-phenyl of **1** rather than the trimethoxy-phenyl of **2**, after the charge delocalization occurring within the absorption event, the former substituent presumably requires deeper changes along the nuclear coordinates (i.e. larger torsions) to give an efficient electronic back-charge transfer. Moreover, *p*DoAO gel is less viscous than *Gemini* gel and its surfactant units comprise only one phenyl ring, with respect to the double ring of each *Gemini* monomer. The aromatic rings of the surfactants are indeed responsible for the π-π interaction with the molecular dye, which results in a hindered charge transfer. The inclusion of **2** in *p*DoAO gel therefore provides the most favorable situation for a partial back-charge transfer mediated by twisting despite the confinement in the gel phase.

All of these findings fully account for the steady-state properties detected in gel: the hypsochromic shift of the fluorescence towards the region of the LE state emission is due to those molecules embedded in the gel phase, which do not evolve to the ICT state and follow the radiative decay channel as a major pathway. Although being a small portion of the total amount, these molecules are blocked in the rigid micellar entanglement and their high fluorescence supposedly overshadows that of the poorly fluorescent molecules placed in the aqueous pools. In fact, the position of the emission spectra of **1** recorded in hydrogels (568 nm in *p*DoAO gel and 565 in *Gemini* gel) is in the region of the LE fluorescence previously observed through femtosecond up-conversion measurements carried out in aqueous solution.[16]

## Experimental

The methyl-pyridinium salts were synthesized as iodide salts following a procedure which has been already described elsewhere.[29,30]

The zwitterionic and cationic surfactants, *p*-dodecyloxybenzyldimethyl N-oxide (*p*DoAO) and bis-[2-(N,N-dimethyl-N-p-dodecyloxybenzylammonium bromide)-ethyl]-ether (*Gemini*) (Chart 2), were used at concentration 0.067 M in deionized water to form homogeneous viscoelastic hydrogels for the immobilization of the substrates, by means of the experimental method that has been previously illustrated.[24,25,31]

Steady–state absorption spectra were recorded with a Perkin Elmer Lambda 800 spectrophotometer, whilst a Fluorolog-2 (Spex, F112AI) spectrophotofluorometer was used to acquire steady-state emission spectra. The latter instrument gives back corrected fluorescence emission spectra taking into account the xenon lamp shape, the monochromator response and the detector sensitivity. Fluorescein, whose $\phi_F$ has been previously found to be 1 in *p*DoAO hydrogel at pH 9,[24] was used as a standard to determine the quantum yields of the molecules in the viscoelastic solutions of both the *p*DoAO and *Gemini* surfactants.

The experimental setup for ultrafast spectroscopic and kinetic measurements has been widely used and described elsewhere.[32-34] Briefly, the 400 nm excitation pulses of ca. 40 fs were generated by an amplified Ti:Sapphire laser system (Spectra Physics, Mountain View, CA). The transient absorption set up (Helios, Ultrafast Systems, Sarasota, FL) is characterized by a temporal resolution of ca. 150 fs and spectral resolution of 1.5 nm. Probe pulses for optical measurements were produced by passing a small portion of the 800 nm light through an optical delay line (with a time window of 3200 ps) and focusing it into a 2 mm thick sapphire window to generate a white-light continuum in the 475-800 nm range. The chirp inside the sample cell was determined by measuring the laser-induced Kerr signal of the solvent. All the measurements were carried out under magic angle conditions, in a 2 mm cell and with an absorbance ranging from 0.3 to 1.0 at 400 nm. The samples were kept in constant movement by a translational sample holder (Ultrafast Systems) controlled by two NSC200 controllers (Newport, Irvine, CA), for horizontal and vertical displacement respectively, to prevent local photodegradation of the non-diffusing medium.

Transient absorption data were analyzed using the Surface Xplorer PRO (Ultrafast Systems)[35,36] and the Glotaran softwares.[37] The first allows to perform the Singular Value Deconvolution of the 3D surface into principal components (spectra and kinetics) followed by Global Analysis (giving lifetimes with an error of ≈10% and Decay Associated Spectra, DAS, of the detected transients).[38] Glotaran was used to perform the Target Analysis assuming either successive steps to describe the evolution of transients accounting for species in a given phase or a parallel mechanism to discriminate the excited state dynamics of those molecules in water from those in the hydrophobic domains of the gel. The Target Analysis allows to carry out the global fit of the acquired data and provides the Species Associated Spectra (SAS), which avoid precursor-successor dynamics of the transients interfering with the calculation of their relative spectral shapes.[37]

## Conclusions

The inclusion of two *push-pull* N-methylpyridinium salts in surfactant hydrogels was studied because of the interesting properties of these organized media. They provide viscous hydrophobic domains made up of intertwined wormlike micelles where they can entrap the investigated molecules, excluding or limiting those deactivation channels involving large amplitude motions usually followed in solution.

The dimethylamino-phenyl and trimethoxy-phenyl derivatives were found to partially distribute between the hydrophobic domains and the aqueous pools of the hydrogels. Those molecules blocked in the gel matrix get much more fluorescent, overshadowing the poor stationary emission of the their counterpart in the water phase. Moreover, femtosecond ESA data and their Target Analysis performed considering a parallel mechanism for molecules placed in the aqueous and gel domains allowed to obtained the exact spectral shape of the different transients. In particular, the Species Associated Spectrum characterizing the gel-permeating molecules matches that of the LE state, proving that the back charge transfer to the ICT state mediated by torsion is almost completely hindered in the viscous medium.

The experiments carried out in hydrogels thus provided a clear-cut proof of the long-debated twisted character of the ICT state of these fluorescent dyes, unraveling their need for torsion in order to get an efficient charge localization in their excited state. The enhancement in their fluorescence quantum yields and excited state lifetimes induced by the rigid hydrogel environment is really promising in view of their possible application as fluorescent probes in medical imaging. At the same time, the NLO properties of these chromophores, such as their two-photon absorption cross sections, would not be diminished by blocking the excited state twisting, with the two-photon absorption process being mainly related to the intramolecular charge rearrangement taking place during the absorption transition. For these reasons, the slowed-down or even hindered formation of the TICT state could enhance the fluorescence properties of these compounds without undermining their NLO response.

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## Notes and references

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By confining two *push-pull* N-methylpyridinium derivatives within the rigid domains of surfactant hydrogels, the twisted nature of their intramolecular charge transfer state (formed in water upon excitation) was unravelled.