

Presence of Two Emissive Minima in the Lowest Excited State of a Push–Pull Cationic Dye Unequivocally Proved by Femtosecond Up-Conversion Spectroscopy and Vibronic Quantum-Mechanical Computations

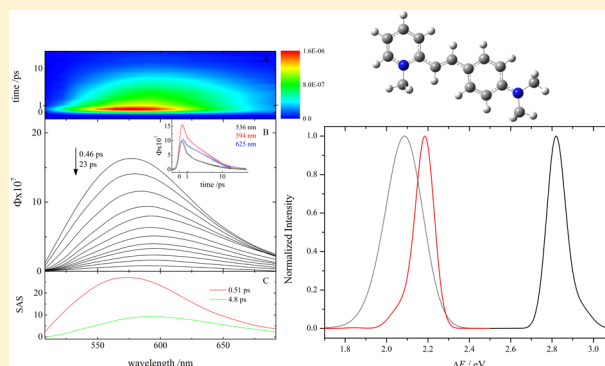
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S Supporting Information

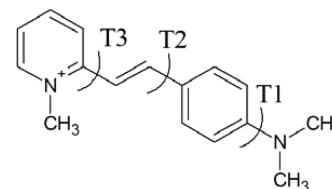
ABSTRACT: The long-standing controversy about the presence of two different emissive minima in the lowest excited state of the cationic push–pull dye *o*-(*p*-dimethylamino-styryl)-methylpyridinium (DASPMI) was definitively proved through the observation of dual emission, evidenced by both experimental (femtosecond up-conversion measurements) and theoretical (density functional theory calculations) approaches. From the fluorescence up-conversion data of DASPMI in water, the time resolved area normalized spectra (TRANES) were calculated, showing one isoemissive point and therefore revealing the presence of two distinct emissive minima of the excited state potential energy hypersurface with lifetimes of 0.51 and 4.8 ps. These spectroscopic techniques combined with proper data analysis allowed us to discriminate the sub-picosecond emitting state from the occurrence of ultrafast solvation dynamics and to disentangle the overlapping fluorescence (very close in energy) of the two components. Vibronic computations based on TD-DFT potential energy surfaces fully confirm those results and provide deeper insights about the key factors playing a role in determining the overall result. The two emissive minima have different structural and electronic characteristics: on one hand, the locally excited (LE) minimum has a flat geometry and an electric dipole moment smaller than the ground state; on the other hand, the twisted-intramolecular-charge-transfer (TICT) minimum shows a rotation of the methylpyridinium moiety with respect to the rest of the structure, and has an electric dipole moment significantly larger than the ground state.



1. INTRODUCTION

Joining state-of-the-art femtosecond spectroscopy and quantum chemical calculations, this work gives an unambiguous explanation for the challenging photophysical behavior of a widely used and well-known cationic dipolar dye, *o*-(*p*-dimethylamino-styryl)-methylpyridinium (DASPMI, Chart 1), unraveling most of the issues that have arisen in decades of experimental and theoretical investigations. Evidence for the presence of two emissive minima in the lowest excited singlet state clearly emerged. Their emissions were found to be close in energy and thus difficult to disentangle without the employment of the powerful fluorescence up-conversion technique. Vibronic computations based on potential energy surfaces obtained by density functional approaches allowed their nature to be identified: a locally excited (LE) state, retaining the planar geometry of the ground electronic state (G) but characterized by a quite low dipole moment, and a highly polar intra-

Chart 1. Chemical Sketch of DASPMI (2-[(*E*)-2-[4-(Dimethylamino)phenyl]vinyl]-1-methylpyridinium Cation), with the Definition of Dihedral Angles of Interest



molecular charge transfer (ICT) state, eventually formed by twisting of the methyl-pyridinium portion.

Received: April 13, 2015

Revised: April 18, 2015

Published: April 22, 2015

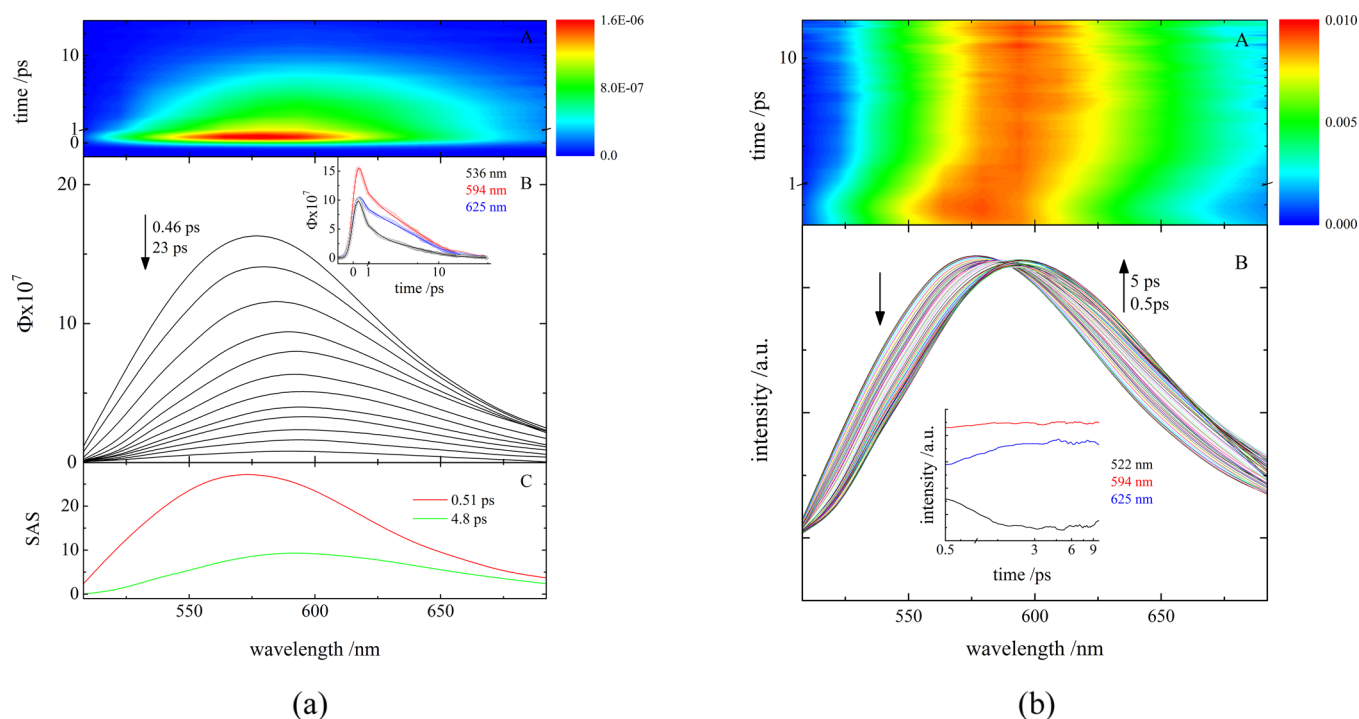


Figure 1. Photophysical characterization of DASPMI in water. (a) Fluorescence up-conversion ($\lambda_{\text{exc}} = 400$ nm): contour plot of the experimental data (A) and time-resolved emission spectra recorded between 0.46 and 23 ps after the laser pulse (B). Inset: decay kinetics recorded at meaningful wavelengths together with the corresponding fitting traces and (C) SAS of the decay components obtained by target analysis. (b) Fluorescence up-conversion ($\lambda_{\text{exc}} = 400$ nm): contour plot of the TRANES (A) and their spectral evolution recorded between 0.5 and 5 ps after the laser pulse (B). Inset: time profile of the TRANES.

Push–pull ionic organic chromophores bearing electron donor (D) and acceptor (A) groups linked by π -conjugated bridges have been scarcely studied in comparison with their neutral counterparts. Dual emission has been revealed in many neutral push–pull compounds^{1–8} characterized by remarkable positive (red shift) fluorosolvatochromism in solvents with increasing polarity⁹ and showing fast ICT upon light excitation.^{10,11} In particular, the analysis of the ultrafast fluorescence data has been instrumental to distinguish between population transfers (such as ICT) and relaxation processes (such as solvation or vibrational cooling), which may take place simultaneously during the excited state deactivation and are thus particularly difficult to discriminate. The detection of rise–decay dynamics in the fluorescence kinetics and of n isoemissive points in the time-resolved area-normalized emission spectra (TRANES) unequivocally point out the existence of $n + 1$ emissive electronic minima.^{12–14} Conversely, in the case of ionic or zwitterionic chromophores showing negative solvatochromism,^{15–18} the involvement of multiple emitting minima in the excited state deactivation is still controversial.^{19–22}

The fluorescence of the cationic push–pull dye DASPMI shows a remarkable dependence on the environment polarity and viscosity,²³ which make it eligible for several applications,^{24,25} such as the design of new smart materials,^{26,27} fluorescence probes for neurons,^{28,29} and other medical and biological applications.³⁰ Furthermore, DASPMI is an efficient molecular system for electronics and nonlinear optics.^{31–33}

Photophysics and photochemistry of DASPMI have been widely investigated with stationary fluorescence and pulse radiolysis, showing that the fluorescence competes with radiationless deactivation, whereas the *trans* \rightarrow *cis* photoisomerization is negligible, at least in polar solvents.^{34,35}

Concerning solvent effects, negative solvatochromism, negligible or slightly positive fluorosolvatochromism, and solvent dependence of the excited state dynamics are reported and discussed in the literature.^{19,36–42} Although the role of an ICT excited state in the relaxation of DASPMI is mostly accepted in the literature,^{21,29,43} its precise electronic nature and its formation mechanism are not clear yet. Photophysical investigations on DASPMI show a complex multifluorescence behavior, within a time-dependent Stokes shift dynamics, whose origin is still unknown. Time-resolved picosecond fluorescence experiments assigned the blue part of the emission spectrum to species fluorescing from the LE state,²² going beyond the common belief that a two-state fluorescence must be reflected by a two-band steady state emission spectrum. In a recent paper,⁴¹ the excited state dynamics of DASPMI was investigated by ultrafast transient absorption spectroscopy. In moderately polar solvents, the charge displacement was found to be slower than the solvent rearrangement (CT controlled), whereas in polar solvents the situation is reversed (solvent controlled) and a fast barrier-less relaxation toward the final ICT state occurs. Although remarkable efforts have been spent to identify the key coordinates ruling the deactivation process, a conclusive and fully convincing picture has not been yet reached.^{21,41,44,45} Additionally, it is still unclear how the charge localizes and fluctuates when a supposedly twisted ICT (TICT) minimum is populated. In spite of preliminary attempts,²¹ reliable quantum mechanical computations including vibronic and environmental effects are not yet available for DASPMI.

2. RESULTS AND DISCUSSION

We report here new femtosecond resolved fluorescence up-conversion measurements of DASPMI in water (experimental

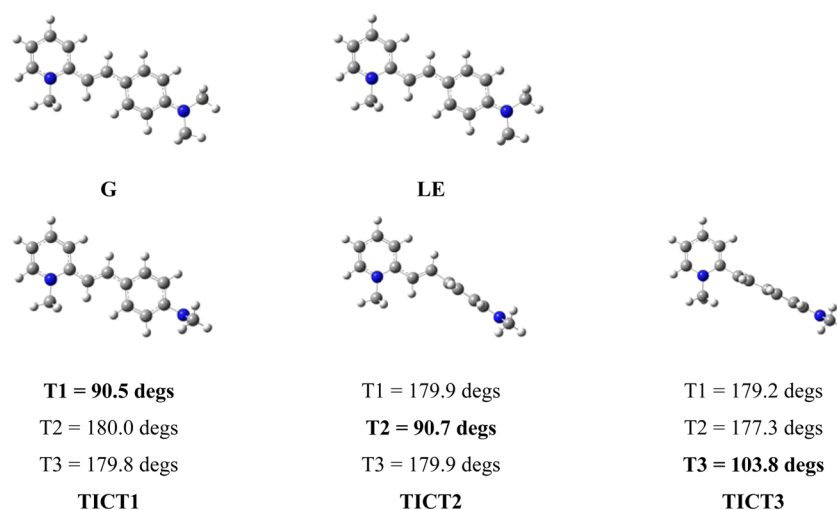


Figure 2. Optimized geometries of G and ES (LE, TICT1, TICT2, and TICT3) minima of DASPMI in water.

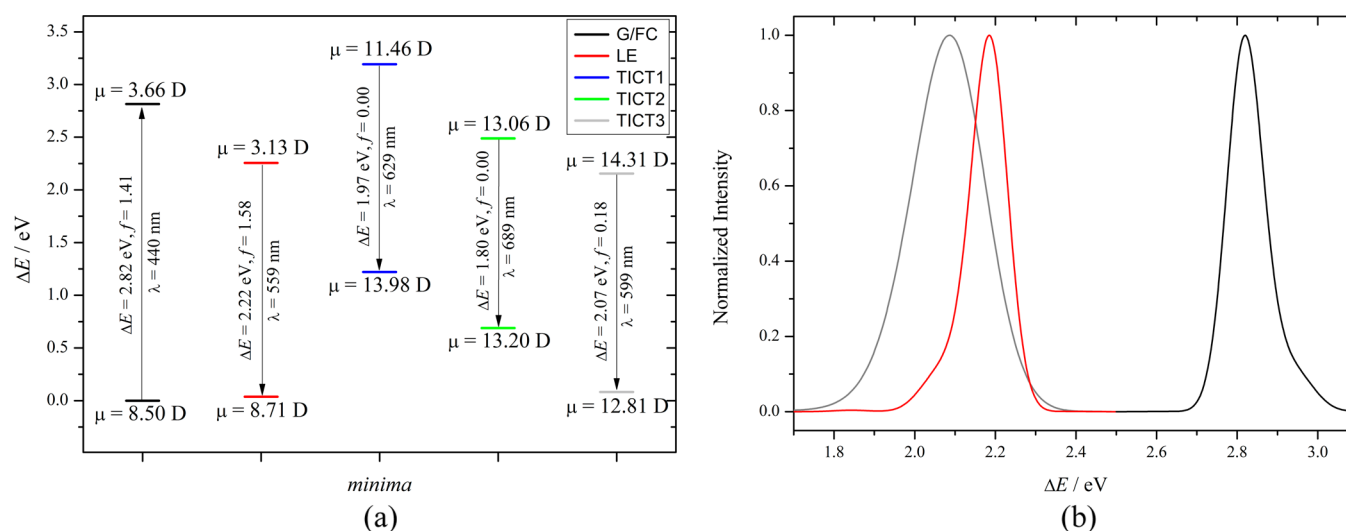


Figure 3. (a) Plot of the energy levels of G and ES (LE, TICT1, TICT2, and TICT3) minima of DASPMI in water. Transition energies (in eV), oscillator strengths, and modulus of electric dipole moments (in D) are also depicted. (b) Vibronic spectra of DASPMI in water. Legend of colors: G absorption spectrum (black), LE emission spectrum (red), TICT3 emission spectrum (gray).

details are described in section SI.1 of the Supporting Information).^{46–48} The time-resolved emission spectra (Figure 1a) undergo a bathochromic shift over time and fully decay in about 20 ps. The best fitting of the data was obtained with a biexponential function, where the two exponential components are considered according to a precursor–successor kinetic scheme (Supporting Information, Figure SI.2a); the lifetimes of the two transients ($\tau_1 = 0.51 \pm 0.05$ ps and $\tau_2 = 4.8 \pm 0.4$ ps) are in full agreement with those previously provided by excited state absorption and assigned to solvent relaxation and to the fully relaxed S_1 state, respectively.⁴¹ Their spectral shapes were obtained through global analysis (decay associated spectra, DAS, shown in the Supporting Information, Figure SI.2b) and target analysis (species associated spectra, SAS, shown in Figure 1a, panel C). The species associated spectra reveal that the fluorescence of the transients is defined by two bands centered at about 565 and 595 nm, respectively, with the latter matching the steady-state emission. This fitting procedure discloses the number of transients and their spectral and kinetic properties, whether they are relaxation processes involved in the excited state dynamics or different emitting species. Both phenomena

imply a progressive red-shift of the fluorescence spectra over time, but the TRANES analysis represents a key tool to discriminate between them: a continuous shift revealed in the TRANES evolution indicates the occurrence of solvent or vibrational relaxation, whereas the observation of n isoemissive points suggests the presence of $n + 1$ emitting species.^{12–14} Figure 1b illustrates the TRANES and their evolution over time. It is clear that right after the formation of the fluorescence signal, at 0.5 ps, an apparent isoemissive point is detected in the TRANES at 594 nm, which is retained during the whole decay process. Instead of a simplistic model based on mere solvation,^{19,20} this finding promotes the idea of a two-state deactivation^{12–14,49} where the first emitting state is completely depopulated within the solvation process (3 ps, cf. concentration profile, Supporting Information, section SI.2, Figure SI.2a), with the formation of a stabilized emitting state. The presence of a rise component in the red side of the TRANES and a decay component with the same time constant in the blue wing is in agreement with a sequential process (sketch in Supporting Information, section SI.3, Figure SI.3b). Similar results were previously obtained for a diphenylamino analogue

of DASPMI:⁴⁹ its TRANES evolution showed two well separated emission bands, whose contributions had previously emerged as a clear enlargement of the stationary fluorescence spectrum in highly polar solvents. It has to be stressed that, in the case of DASPMI, the employment of fluorescence up-conversion allowed two distinct emissions to be identified although very close in energy (their maxima differ by just 30 nm), providing us with a satisfactory explanation for its non-solvatochromic steady-state fluorescence.

A mechanistic interpretation of the experimental observations was gained by vibronic computations based on density functional potential energy surfaces of the key electronic states including bulk solvent effects by means of the polarizable continuum model (PCM). The results are summarized in Figure 2, whereas the computational details are described in section SI.4 of the Supporting Information. In detail, the optimized geometry of the ground electronic state (G) is planar, and a local minimum (locally excited, LE) of the first excited singlet (S1) was found retaining full planarity. However, other local minima of S1 (hereafter TICT1, TICT2, and TICT3) were characterized in terms of different values of the dihedral angles T1, T2, and T3 (Chart 1). The relative energy and the electronic properties of all minima are sketched in Figure 3a. In aqueous solution, LE and TICT3 are the only structures with non-vanishing oscillator strengths for emission. In the gas phase, however, only LE has appreciable emission oscillator strength, and its absorption and emission energies are very close. (Data referring to the gas phase are reported in section SI.5 of the Supporting Information.) While the electric dipole moment of LE is similar to that of the molecule after vertical excitation (in FC region), when relaxing toward the TICT3 minimum, a remarkable charge reorganization is found, and the dipole moment significantly increases. The vibronic spectra for the $G \rightarrow FC$ absorption together with the $LE \rightarrow G^*_{LE}$ and $TICT3 \rightarrow G^*_{TICT3}$ emissions (Figure 3b) well reproduce the experiments, and show that the vibronic bands exhibit an asymmetric broadening (fwhm = 0.11, 0.12, and 0.21 eV and asymmetry parameter⁵⁰ $\delta_{1/2} = 0.04, 0.04, \text{ and } 0.07$ eV for the three transitions, respectively).

3. CONCLUSIONS

The converging results of experimental and quantum chemical approaches allowed us to obtain for the first time a comprehensive and reliable picture of the excited state dynamics of DASPMI. The fluorescence up-conversion measurements and the TRANES analysis in particular proved to be extremely valuable for unraveling the existence of a sub-picosecond emitting state, otherwise masked by ultrafast solvation processes, later evolving into a second emissive state (the fully relaxed S_1). The quantum mechanical results corroborated this finding, disclosing the photoinduced structural and electronic evolution undertaken by DASPMI: after the initial excitation to FC, the system evolves toward a shallow minimum (LE) with significant emission probability. The structural deformations via T1, T2, and T3 torsions lead to three possible twisted ICT states characterized by different charge localizations and conformations (TICT1, TICT2, and TICT3). Among them, the only one still able to emit is the lowest-lying TICT3 formed through rotation of the methylpyridinium moiety.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, global and target analysis, concentration profiles and phenomenological kinetic picture, computational details, energy levels, and their properties *in vacuo*. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.5b03545.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge support from the Italian “Ministero per l’Università e la Ricerca Scientifica e Tecnologica”, MIUR (Rome, Italy), under the FIRB “Futuro in Ricerca” 2013, no. RBFR13PSB6, and PRIN “Programmi di Ricerca di Interesse Nazionale” 2010–2011, no. 2010FM738P. The staff of the “DreamsHPC” super-computing laboratory at the Scuola Normale Superiore is thanked for computational facilities and technical support. The authors are grateful to Prof. Ugo Mazzucato for useful discussions.

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