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Intramolecular photo-driven charge transfer in a series of pyridyl substituted phenyloxazoles. Structural relaxation in meta-substituted ethylpyridinium derivative of phenyloxazole

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Abstract

A series of pyridyl (pyridinium) substituted benzoxazoles were studied by steady state absorption, fluorescence spectroscopy, time-resolved fluorescence spectroscopy, fs pulse absorption and polarization spectroscopy, and quantum-chemical calculations. The spectral and kinetic parameters of the fluorophores in MeCN and EtOAc were obtained experimentally and were calculated by means of DFT and TDDFT methods. A scheme including four transient excited states was proposed for the interpretation of differential absorption kinetics of the charged fluorophores. Expressions describing the actual kinetics graphs, the decay associated spectra, and the species-associated spectra were derived. The charge shift step was found to be dependent on average solvation times. A charge shift followed by the formation of the twisted conformer was found for the excited 1-ethyl-3-(5-phenyloxazol-2-yl)pyridinium 4-methyl-1-benzenesulfonate in MeCN and EtOAc. Conformational analysis confirms a large amplitude motion of the meta-substituted ethylpyridinium group as an additional structural relaxation path producing an abnormally large fluorescence Stokes shift.

Graphic abstract



Keywords Pyridyl substituted phenyloxazole · Charge shifted state · Twisted state · Transient absorption

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1 Introduction

Pyridyl-substituted phenyloxazoles were used earlier as model compounds for the study of static and dynamic intermolecular proton transfer [1]. The $N(CH_3)_2$ -substituted oxazole-oxadiazoles were seen as organic luminophores with an abnormally large fluorescence Stokes shift (up to

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14,700 cm⁻¹ in MeCN) [2]. 2-Phenylbenzoxazole (PBO), 2,5-diphenyloxazole (PPO) [3] and 2-(4-pyridyl)-5-phenyloxazole (4PyPO) [4] were used as laser dyes. It was shown, that the sterically hindered *ortho* analogues of 1,4-bis(5phenyloxazol-2-yl) benzene (POPOP) underwent noticeable flattening in their excited singlet state without significant radiationless loss of excitation energy. The flattening in the excited state is responsible for lowering the energy of the fluorescent state, leading to an abnormally large Stokes shift [5]. Recently, a series of novel organosilicon-based molecular antennas was developed starting from phenyloxazole derivatives [6]. Intramolecular charge transfer (ICT) accompanied by the twisting of the benzthiazole moiety versus the dimethylaminobenzene moiety proceeds efficiently for the thioflavin T cation (ThT) in low-viscosity solvents [7].

In our earlier work, the spectral-luminescence behavior of pyridyl-substituted benzoxazoles was studied via steadystate absorption and fluorescence spectroscopy at 293 and 77 K as well as fluorescence spectroscopy at increased pressure (up to 4.5 kbar) [8]. Viscosity and temperaturedependent relaxation was discovered for several protonated (ethylated) cations of hetarylazoles. In this study, pyridylsubstituted phenyloxazoles are analyzed via time-resolved fluorescence spectroscopy, femtosecond transient absorption spectroscopy, and density functional theory calculations (DFT, TDDFT). It was vital to figure out how the charge of the fluorophore, the position of the nitrogen atom in the pyridyl (pyridinium) moiety, and the solvent itself affect the spectral and kinetic behavior, steering ICT, and defining the type of structural relaxation. Uniquely among other available experimental approaches, femtosecond transient absorption spectroscopy was used to determine the entire relaxation pathway. Time-resolved anisotropy measurements were additionally used to detect structural mobility in the excited fluorophores.

2 Experimental

The measurements were carried out with freshly prepared aerated solutions of the fluorophores in MeCN ("Fisher", HPLC gradient grade, water content 0.0021%) and ethyl acetate (chemically pure grade). Beforehand, trace water and acid were removed from ethyl acetate via double distillation with K₂CO₃ and CaH₂. Steady-state absorption spectra were recorded on a Shimadzu-3100 spectrophotometer. Quantum-corrected fluorescence spectra were measured with a Perkin-Elmer LS-55 spectrofluorometer. Fluorescence quantum yields were determined relative to quinine sulfate in 1.0 N H₂SO₄ (φ_f =0.546, [9]) with equal absorbances at the excitation wavelength. 3-(5-Phenyloxazol-2-yl)pyridine (1) [10, 11], 4-(5-phenyloxazol-2-yl)pyridine (2), 1-ethyl-3-(5-phenyloxazol-2-yl)pyridinium 4-methyl-1-benzenesulfonate

(1a), and 1-ethyl-4-(5-phenyloxazol-2-yl)pyridinium 4-methyl-1-benzenesulfonate (2a) were used as received [12]. The structures of compounds are shown in Fig. 1.

2.1 Fluorescence kinetics

Singlet excited state fluorescence decays were measured with Fluotime 300 Time-Correlated Single Photon Counting (TCSPC) UV-IR spectrofluorimeter (Picoquant GmbH). The samples were excited by a 600 ps diode pulse at 320 nm (PLS PicoQuant), 10 MHz iteration frequency with a vertically polarized beam. Emission was detected with a magic angle polarizer to prevent undesired polarization effects. The obtained fluorescence decay curves were analyzed using FluoFit software (PicoQuant). The data sets were subjected to global analysis with FluoFit software (FluoFit Manual, PicoQuant, 2017) to resolve components with different lifetimes.

2.2 Femtosecond transient absorption

Femtosecond transient absorption (TA) spectra were measured at 295 K with a pump and light supercontinuum probe setup with a 3.33 fs delay step and a 0.5 nm wavelength step. The spectra were subjected to a correction procedure. The details of transient spectra measurements were described in our prior paper [13]. The characteristic times (τ_i) were calculated using global analysis of the TA spectra in the appropriate time range. The calculations were carried out using the standard Origin 7.0 and MATLAB 6.0 functions. Since the experimental flash function convolution (FWHM=30 fs) with monoexponential decay ($\tau = 50-80$ fs) changes the τ_i value by only 1–3%, the experimental TA spectra were processed without deconvolution. The average measurement error was ~5%.



Fig. 1 Molecular structures of the fluorophores

2.3 Quantum chemical calculations

Quantum chemical calculations were performed using the GAMESS (US) [14] program package with the 6-31G(d,p) basis set. The geometry of the compounds in the ground state was optimized by means of DFT; the excited state geometry was optimized by means of TDDFT (CAM-B3LYP functional). The environmental effects were included via the Solvation Model Density continuum model [15]. Absorption and emission spectra were calculated using the Firefly v.8.2 program package [16] by means of state-averaged complete active space self-consistent field (SACASSCF) improved by second-order quasi-degenerate perturbation theory (XMC-QDPT2) [17]. The medium effects were included via the dielectric polarizable continuum DPCM model [18]. The active space included 10 electrons in 8 orbitals (for 1 and 2) and 14 electrons in 11 orbitals (for 1a and 2a). The density matrix was averaged by 9 lowest singlet states.

3 Absorption and fluorescence study

In the absorption spectra of 1, 1a, 2, and 2a in MeCN and EtOAc, a well-defined longwave band and a less intensive shortwave band can be found (Fig. 2a). In all the cases, the energy gap between them is substantial. The fluorescence spectrum of the fluorophores in MeCN and EtOAc consists of a single smooth band. The positions and the shapes of the fluorescence bands are independent of the excitation wavelengths within a wide spectral range (Fig. 3). The fluorescence excitation spectra of 1, 1a, 2, and 2a in MeCN and EtOAc, detected at different wavelengths, are analogous to the corresponding absorption spectra. Small rise in a ratio of intensities of long versus short wavelength fluorescence excitation bands of 1a (from 450 to 530 nm) and 2a (from 550 to 480 nm) is explained by measurement error (Fig. 3). The absorption and fluorescence spectra of the cations are red-shifted versus the neutral compounds (Fig. 2a, Table 1). The E_{00} values for **1a**, **2a** in both solvents are lower than those for 1, 2. Compared with other compounds, the 1a cation was characterized by the smallest fluorescence quantum yields (φ_f) and the largest $\Delta_a(1/2)$ and $\Delta_f(1/2)$ (FWHM) values. Its fluorescence Stokes shift $(\Delta \tilde{v}^{a-f})$ is also abnormally large (Table 1). This feature points to a specific photorelaxation process, resulting in moderate fluorescence quenching. This relaxation does not correspond to the solvent polarity function (Table 1): $f(\varepsilon_0, n) = 0.71$ (MeCN), 0.4 (EtOAc) [19]. The solvatochromic data [8] demonstrates that the dipole moment changes only moderately for 1, 1a, 2, and 2a upon excitation (3.1, 3.8, 6.7, and 5.6 D, respectively). The emitting state of neutral and charged fluorophores is either a moderate charge transfer (CT) or a charge shifted (CS) state where the charge has been transferred from the oxazole



Fig. 2 Absorption and fluorescence spectra of **1**, **1a**, **2**, and **2a** in MeCN at 293 K (*a*). The relative areas in the fluorescence spectra were equal to the ratios of the corresponding φ_f values. The fits for the fluorescence decays of **1**, **1a**, **2**, and **2a** in MeCN at 22 °C were monoexponential (*b*). Excitation wavelength: 330 nm. Below. The residuals' autocorrelation function for **1** is shown as an example. $C(t_j) = \left(\frac{1}{m}\sum_{k=1}^{m} D_k D_{k+1}\right) / \left(\frac{1}{n}\sum_{k=1}^{n} D_k^2\right)$, where D_k is the deviation in the *k*th data point and D_{k+d} is the deviation in the *k*+*j*th data point [20]

group to the pyridine (pyridinium) acceptor. The rise in the fluorescence quantum yields of **1a**, **2a** (up to 0.95, 0.85 in EtOH in the 293–77 K range [8]) allows us to suggest, that the main deactivation channel at ambient temperature is internal conversion.

4 Fluorescence decay times

The fluorescence decay kinetics of **1**, **1a**, **2**, and **2a** in MeCN are shown in Fig. 2b. All the decay plots were fitted monoexponentially. The τ values are independent of the λ_{exc} values. The analogous kinetic data in EtOAc have similar values (Table 1). The τ values of the cations are 1.9–2.74 (MeCN)



Fig. 3 Fluorescence excitation spectra (left) and fluorescence spectra (right) of **1a** in MeCN at 293 K at different observation and excitation wavelengths, respectively

and 1.7–2.1 (EtOAc) times higher than those for neutral molecules (Table 1). The **1a** cation has the smallest k_f . The k_d values of **1**, **1a** with meta-substituted pyridyl nitrogen are 3.3–5.8 times higher than those for **2**, **2a** with para-substituted nitrogen atoms. Obviously, there is no necessary correlation between the higher k_d values and specific relaxation.

5 Transient absorption study

Detecting of TA spectra in solvents of different polarities is useful when ICT is studied. This is also helpful when spectral evolution proceeds over several stages and the whole relaxation pathway can be revealed. Upon excitation by a 30 fs pulse at 330 nm, in the TA spectra of 1 and 2 in MeCN, the following occurs. During the first 350 fs and 320 fs, respectively, a single narrow band arises at ~501 and 493 nm, respectively. After the saturation stage (up to ~1 ps), the TA band of 1, 2 was subjected to partial quenching up to 500 ps. The spectral evolution of 1 and 2 in EtOAc is similar. For 1a and 2a in MeCN during the first 160 fs and 210 fs, respectively, a single TA band arises at ~467 nm and 460 nm. Then, within 160–350 fs for **1a** and 210–350 fs for **2a**, the band transforms into a widened blue-shifted band $[\Delta \lambda_a^{\max} = 35 \text{ nm} (1a), 31 \text{ nm} (2a)]$. In both cases, distinct isosbestic points were observed. After the saturation stage (up to ~2 ps), the TA bands of **1a** and **2a** were subjected to weak quenching (up to 500 ps). The corresponding TA spectra of **1a** in EtOAc show similar transformations (Table 2). Partial time sequences of the spectral evolution of **1a** and **2a** in MeCN with a precursor–successor relationship were shown in Fig. 4a, b.

The results of global analysis showed that the TA spectra of **1a** (**2a**) in MeCN and **1a** in EtOAc can be represented as a sum of 3 exponential plots with a residual term (Table 2). We propose a relaxation pathway for **1a** (**2a**) after excitation that involves 4 excited transient states and proceeds via 4 stages (Scheme 1). These are, in order: ultrafast internal conversion of a hot local excited state (LE* \rightarrow LE), the formation of a solvent-dependent charge-shifted state (LE \rightarrow CS*), relaxation to a fluorescent CS state (CS* \rightarrow CS) with subsequent slow deactivation to the ground state (CS \rightarrow GS).

Despite the meta substituted derivative **1a** in S_0 manifesting as two conformers with dihedral angles of $\Theta = 0^\circ$ and 180°, respectively (see next section, Fig. 6a), it is not necessary to introduce a separate kinetic interpretation for **1a**. The absorption and fluorescence spectra of these closely related conformers are indistinguishable (Fig. 3) and we can satisfactorily approximate the excitation of 2 conformers as affecting a single species for the para substituted derivative **2a**.

The calculated characteristic times (τ_1 , τ_2 , τ_3) are shown in Table 2. Higher values estimated for τ_3 are probably related to vibrational cooling in the solvent. According to Scheme 1, the following 4 differential equations are valid:

$$\frac{\mathrm{d}[\mathrm{LE}*]}{\mathrm{d}t} = bE(t) - k_1[\mathrm{LE}*],\tag{1}$$

$$\frac{\mathrm{d}[\mathrm{LE}]}{\mathrm{d}t} = k_1[\mathrm{LE}*] - k_2[\mathrm{LE}],\tag{2}$$

Table 1 Spectral-kinetic parameters of fluorophores in MeCN (top) and EtOAc (bottom) at 293 K

Agent	$\tilde{v}_a^{\text{max}}/\text{cm}^{-1}$	$a\Delta_a(1/2)/cm^{-1}$	$\tilde{\nu}_{\rm f}^{\rm max}/{\rm cm}^{-1}$	$^{a}\Delta_{f}(1/2)/cm^{-1}$	$arphi_{ m f}$	E_{00}/cm^{-1}	$\Delta \tilde{v}^{a-f}/cm^{-1}$	^b τ/ns	$k_{\rm f} \times 10^{-8} / {\rm s}^{-1}$	$k_{\rm d} \times 10^{-8} / {\rm s}^{-1}$
1	32,470	5800	26,455	4230	0.804	29,090	6250	1.63	4.94	1.21
	32,470	5670	26,740	4280	0.890	29,170	5980	1.48	6.00	0.74
1a	30,400	6870	18,800	4690	0.165	24,230	12,070	4.46	0.37	1.87
	30,670	6820	18,730	4880	0.086	25,230	12,350	3.11	0.28	2.98
2	31,650	5690	25,970	3930	0.938	28,570	5910	1.67	5.63	0.37
	31,350	5780	26,280	3960	0.890	28,750	5240	1.39	6.42	0.79
2a	26,810	4550	20,700	3010	0.898	23,480	6260	3.18	2.83	0.32
	27,470	4760	20,600	3530	0.519	24,040	7020	2.40	2.16	2.00

^aFull width at half maximum (FWHM) of the absorption ($\Delta_a(1/2)$) and fluorescence ($\Delta_f(1/2)$) spectra ^bmeasurement error < 0.01 ns

vgent	$\lambda_{\rm a}^{\rm max}/$	uu		$\lambda_{ m isos}^{ m max}/ m nm$	$ au_1/\mathrm{ffs}$	$ au_2/\mathrm{fs}$	$ au_3/\mathrm{Fs}$		$k_1 \times 10^{-13} / \mathrm{s}^{-1}$	$k_2 \times 10^{-13}$ /s ⁻¹ $k_3 \times 10^{-12}$ /s ⁻¹
	501	I	I	50	I		388	2.0	I	°2.6
	504	I	I	31	53.	3	1709	3.2	°0.2	9.0°
а	$^{a}467 \rightarrow 432$		~ 452	35	87		543	2.9	1.2	1.8
	$472 \rightarrow 450$		I	45	10	6	982	2.2	0.9	1.0
	493	I	I	56	Ι		353	1.8	I	°2.8
	498	I	I	37	17	1	1230	2.7	9.0°	°0.8
в	$460 \rightarrow 429$		~450	40	15.	5	668	2.5	0.6	1.5
	р Г	I	Ι	I	Ι		I	I	I	I

For 1 and 2 instead of SC* and SC states (Scheme 1) LE₁ and LE₂ states should stand

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$$\frac{d[CS *]}{dt} = k_2[LE] - k_3[CS *],$$
(3)

$$\frac{d[CS]}{dt} = k_3[CS *] - (k_f + k_d)[CS],$$
(4)

where bE(*t*) is the excitation function (taken as zero), $k_f + k_d$ is the sum of deactivation rate constants of the fluorescent CS state (Table 1). It should be noted that $k_f + k_d << k_3$ for all the described cases. This allows us to simplify the resulting equations, supposing that $(k_f + k_d)[CS] \rightarrow 0$. Using Eqs. 1–4 it is easy to work out the expressions for differential absorption kinetics of each state involved in the relaxation process:

$$\Delta D_{\text{LE}*}(\lambda, t) = \varepsilon_{\text{LE}*}(\lambda)[\text{LE}_0 *]e^{-k_1 t},$$
(5)

$$\Delta D_{\rm LE}(\lambda, t) = \varepsilon_{\rm LE}(\lambda) [\rm LE_0 *] \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}), \qquad (6)$$

$$\Delta D_{\mathrm{CS}*}(\lambda, t) = \varepsilon_{\mathrm{CS}*}(\lambda) [\mathrm{LE}_0 *] \frac{k_1 k_2}{(k_1 - k_2)(k_1 - k_3)(k_2 - k_3)} ((k_2 - k_3) \mathrm{e}^{-k_1 t} - (k_1 - k_3) \mathrm{e}^{-k_2 t} + (k_1 - k_2) \mathrm{e}^{-k_3 t}),$$
(7)

$$\frac{\Delta D_{\rm CS}(\lambda,t) = \varepsilon_{\rm CS}(\lambda)[\rm LE_0 *]}{\frac{X - k_1 k_2 (k_1 - k_2) e^{-k_3 t} + k_1 k_3 (k_1 - k_2) e^{-k_2 t} - k_2 k_3 (k_1 - k_2) e^{-k_1 t}}{X},$$
(8)

$$\mathbf{X} = (k_1 - k_2)(k_1 - k_3)(k_2 - k_3).$$
(9)

Using the material balance equation $[CS] = [LE_0^*] - [LE] - [CS^*]$, we discovered that total differential absorption can be described as a sum of 4 terms: 3 of them exponential and a residual term without exponential functions: $\Delta D_{\text{total}}(\lambda, t) = (\varepsilon_{\text{LE}^*}(\lambda) - \varepsilon_{\text{LE}}(\lambda))[LE^*] + (\varepsilon_{\text{LE}}(\lambda) - \varepsilon_{\text{CS}}(\lambda))[LE] + (\varepsilon_{\text{CS}^*}(\lambda) - \varepsilon_{\text{CS}}(\lambda))[CS^*] + \varepsilon_{\text{CS}}(\lambda)[LE_0^*]$. Therefore, the residual term, necessitated using global analysis, can be represented as $\varepsilon_{\text{CS}}(\lambda)[LE_0^*]$. Using the decay associated spectra (DAS) easily derived from Eqs. 5–9 for each characteristic time together with the residual term we can identify the spectra of each individual state involved in the relaxation (species associated spectra—SAS). They can be described by simple expressions 10–13:

$$\Delta D_{\text{LE}*}(\lambda) = \varepsilon_{\text{LE}*}(\lambda)[\text{LE}_0^*] = A_0(\lambda) + A_1(\lambda) + A_2(\lambda) + A_3(\lambda),$$
(10)
(*h* = *h*)A_1(\lambda) + (*h* = *h*)A_1(\lambda)

$$\Delta D_{\rm LE}(\lambda) = \varepsilon_{\rm LE}(\lambda) [\rm LE_0^*] = A_0(\lambda) + \frac{(k_1 - k_2)A_2(\lambda) + (k_1 - k_3)A_3(\lambda)}{k_1},$$
(11)

$$\Delta D_{\rm CS*}(\lambda) = \varepsilon_{\rm CS*}(\lambda) [\rm LE_0^*] = A_0(\lambda) + \frac{(k_1 - k_3)(k_2 - k_3)A_3(\lambda)}{k_1 k_2},$$
(12)

Fig. 4 Differential absorbance of 1a within 0.17–0.35 ps after excitation in MeCN (*a*). Differential absorbance of 2a within 0.21–0.35 ps after excitation in MeCN (*b*) Excitation pulse: 30-fs at 330 nm, increment: 10 fs, insets: concentration curves for 1a and 2a obtained from Eqs. 5–9. Species associated spectra (SAS) of (1a, (*c*) and (2a, (*d*)) obtained from Eqs. 10–13





 $\mbox{Scheme 1}$ The main relaxation pathway of $\mbox{1a}$ (2a) in MeCN and 1a in EtOAc

$$\Delta D_{\rm CS}(\lambda) = \varepsilon_{\rm CS}(\lambda)[\rm LE_0^*] = A_0(\lambda). \tag{13}$$

where $\varepsilon_{LE^*}(\lambda)$, $\varepsilon_{LE}(\lambda)$, $\varepsilon_{CS^*}(\lambda)$, $\varepsilon_{CS}(\lambda)$ are the molar absorption coefficients in S_1 ; $A_0(\lambda)$ is the residual term; $A_1(\lambda), A_2(\lambda), A_3(\lambda)$ are the corresponding preexponential terms. The calculated SAS for **1a** (**2a**) in MeCN are shown in Fig. 4c (d). It is evident that the presence of a large negative band of stimulated emission (SE) in the TA spectra of **2a** (Fig. 4b) is reflected in the corresponding SAS (Fig. 4d).

As for neutral fluorophores 1, 2, the LE \rightarrow CT process does not manifest itself in the TA spectra in MeCN. In other words, the characteristic times τ_2 were not resolved. This observation contradicts the solvatochromic data, which undoubtedly reveal the presence of a moderate charge transfer process for all the fluorophores. Contrary to the 3-exponential fitting for the TA spectra of 1 and 2 in EtOAc, the resulting SAS do not contain distinct, blue-shifted CT spectra: instead, two sorts of LE spectra were observed.

The emission and absorption polarization measurements can provide insight into the intramolecular motion of various amplitudes: rotation, bending, rehybridization, etc. [21]. When torsional motion is observed on a timescale that is comparable



Fig. 5 Transient absorption anisotropy r(t) of **1a** in MeCN at 467 nm measured within 10–300 ps. Excitation with a 30-fs pulse at 330 nm, increment: 1 ps. The red curve represents monoexponential fitting: $y=0.4\exp(-t/37.04)$

to the rotational diffusion of the solute as well as the effects on the angle (Θ) between the Frank–Condon ($M_{\rm FC}$) and the relaxed ($M_{\rm f}$) emission transition moments, the r(t) curve should involve an additional decay component. However, the r(t) data obtained for **1a** in MeCN (EtOAc) were too scattered to resolve a complex decay. Figure 5 includes the monoexponential fitting of the anisotropy from 0.4 (Θ =0) to zero ("magic angle" Θ ~54.7) with a characteristic rotation time of φ =37.0 (57.6) ps. Using a simple rigid sphere model ($\varphi = V\eta/kT$, where V is the volume of the solvated sphere, η is solvent viscosity at 293 K [3.57×10⁻⁴ Pa·s (MeCN) and 4.58×10⁻⁴ Pa s (EtOAc)] we get Fig. 6 Conformational curves for **1a** (*a*, *c*) and **2a** (*b*, *d*) in MeCN in the ground and excited states. Θ is the dihedral angle between the pyridinium and oxazole moieties (xMC-QDPT2); Ω is the dihedral angle between the phenyl and oxazole moieties [MP2 (black circle), S₀; CAMB3LYP (red circle), S_1 ; CAMB3LYP (black and red triangles), S_0 and S_1 ; xMCQDPT2 (black and red squares), S_0 and S_1]



the radii of the rotating species of 4.7 Å and 5.0 Å, respectively.

the efficient radius of a twisting phenyl group is equal to 1.2 Å



Fig. 7 Two HOMOs and LUMOs calculated for 1a (top) and 2a (bottom) in MeCN. HOMO-2 is the second occupied orbital from the top; LUMO-2 is the second unoccupied orbital from the bottom

These data point to the fluorophore rotating as a whole, because

[22]. According to DFT calculations, the maximal interatomic

Table 3 Calculated spectral- energy parameters of	Agent	$E_{S_0 \rightarrow S_1}$ /cm ⁻¹	$f_{S_0 \to S_1}$	$E_{S_0 \rightarrow S_2}$ /cm ⁻¹	$f_{S_0 \to S_2}$	μ_0/D	μ_1/D	μ_2/D
fluorophores in MeCN [B3LYP (top)/xMCQDPT2 (bottom)]	1	32,990 33,790	0.4 0.4	37,340 37,420	0.001 0.004	4.5 4.5	19.5 19.1	5.4 5.5
	^a 1a	26,050/26,010 26,700/26,550	0.07/0.11 0.18/0.23	29,600/29,750 29,760/29,910	0.23/0.19 0.2/0.15	15.2/16.4 15/16.2	10.9/11 8.5/8.1	6.5/6.6 5.6/5.1
	2	32,020 32,580	0.35 0.42	38,630 37,670	0.003 0.009	4.1 4.2	22.7 21.4	7.1 7.4
	2a	25,160 26,130	0.27 0.56	29,760 34,520	0.009 0.013	15.9 16.1	8.4 2.9	17.7 11.5

^aValues before and after slash correspond to the conformers with $\Theta = 0^{\circ}$ and 180°, respectively

radius of **1a** is 6.1 Å. A small discrepancy is observed due to the elongated (namely, elliptical) shape of the fluorophore. Analogous anisotropy measurements for a more compact molecule **1** in MeCN gave a value of effective radius of 4 Å.

6 Quantum-chemical calculations

According to quantum chemical calculations, the fluorophores **1**, **2** in MeCN exist as planar conformers in the ground state. It is also mostly true for **1a** and **2a**, barring the non-planar location of the ethyl groups and twisted (up to $30^{\circ}-40^{\circ}$) disposition of the phenyl groups. Upon the excitation of **1a**, the electron density is redistributed from the HOMO-1 localized on the oxazole donor to LUMO-1 ($S_0 \rightarrow S_1$) or LUMO-2 ($S_0 \rightarrow S_2$), localized on the pyridinium acceptor (Fig. 7). The two absorption bands of **2a** are HOMO-1 \rightarrow LUMO ($S_0 \rightarrow S_1$) and HOMO-2 \rightarrow LUMO ($S_0 \rightarrow S_2$).

Generally, the $E_{S_0 \to S_1}$ parameters correspond to the experimental absorption maxima of the fluorophores (\tilde{v}_a^{max}) in MeCN quite well (Tables 1, 3). The calculations show that the experimental longwave absorption band of **1a** in MeCN corresponds to $S_0 \to S_2$, not to $S_0 \to S_1$. On the other hand, Gaussian shape of this band (Fig. 2a) implies that the actual oscillator strength value ($f_{S_0 \to S_1}$) should be much lower. Thus, the determined $f_{S_0 \to S_n}$ parameters should be used cautiously. The angles between the transition moments in S_0 and S_1 (S_2) approach 170°–180° which should increase the contribution of a reorientational term of the solvent relaxation in the observed evolution of the TA spectra.

The conformational curves found for **1a** in MeCN show that in the ground state the solute involves practically equal population of 2 conformers with $\Theta = 0^{\circ}$ and 180° (Fig. 6a). The first conformer has a slightly larger oscillator strength value $(f_{S_0 \to S_2})$ (Table 3). In the excited S_1 state, the twisted position of the ethylpyridinium moiety becomes slightly favorable for each conformer in terms of energy. A relatively small gap of 0.6 eV between these states allows us to propose fast $S_2 \to S_1$ conversion upon the excitation of **1a**. The relaxation is barrierless and the energy minimum corresponds to 40° and 140° . This is not the case for **2a** (Fig. 6b) where the planar molecular structure persists. Additionally in Fig. 6a, b the S_0-S_1 energy gap for the relaxed state of the metasubstituted cation **1a** becomes noticeably smaller than the gap for the para-substituted cation **2a** ($\Delta E(S_0-S_1)=0.48$ eV). This observation is based upon the phenomenon known as the Zimmerman meta effect in organic photochemistry [23].

The twisting on the phenyl side of the fluorophores was analyzed with DFT (CAMB3LYP) calculations. In the ground state, the value of the dihedral angle between the phenyl and the oxazole moieties is less than 13°. The MP2 method gives a larger angle (~25°). On the other hand, the energy gain for such conformers is negligible (<0.01 eV, Fig. 6c) and the solute represents a population of planar and slightly twisted forms. A similar picture is also observed for the other fluorophores. For **1a** and **2a**, a totally planar dihedral angle between the phenyl and the oxazole moieties becomes energetically favorable in the excited singlet state (Fig. 6c, d). Thus, the structural photorelaxation on the phenyl side is represented by the planarization of slightly twisted conformers.

7 Discussion

As said above, the spectral evolution of 1a and 2a in MeCN and EtOAc involves a separate second step, the formation of a blue-shifted TA band showing a distinct precursor-successor relationship (this is absent in the spectra of 1, 2). The timespans of this step for 1a (2a) in MeCN [160 (210 fs)-350 (350 fs)] and for **1a** in EtOAc (150-1.0 ps) are comparable with average solvation times of MeCN and MeOAc (260 fs, 850 fs, [19]). Apparently, what we can observe here is the intramolecular $LE \rightarrow CS$ process, governed by the solvent. As was recently shown, the TA spectra of several DMABN-related donor-acceptor compounds also demonstrate pronounced blue shifts of the TA spectra in MeCN [24]. Although the $\Delta \mu$ values of 1, 2, 1a, and 2a are similar, we do not observe noticeable blue shifts in the TA spectra of neutral compounds 1, 2 (probably due to weaker dipole-dipole vs. ion-dipole interactions).

The abnormally large Stokes shift observed for **1a** may be related to larger changes in the total solvation energy upon the excitation of the cation. However, the E_{00} values of **1a** and **2a** are close (Table 1). Also the Stokes shift can be increased due to larger ground state solvation (repulsion) energy (δE_{rep}) [25]. Most likely, this shift owes to additional relaxation which is shown in Fig. 5a for **1a**. According to TDDFT calculations, this path represents structural relaxation for the ethylpyridinium group (planar to twisted). Apparently, the driving force of this large amplitude motion originates from the asymmetry of the corresponding LUMOs in the 3-ethylpyridinium moiety (vs 4-ethylpyridinium),

$$A^{+}-D \xrightarrow{\text{excitation}} (A^{+}-D)^{*} \xrightarrow{\text{charge shift}} (A^{\bullet\delta+}-D^{\delta+})^{*} \xrightarrow{\text{twisting}} (A^{\bullet\delta+}-D^{\delta+})^{*}$$

Scheme 2 Dual relaxation pathway of 1a in MeCN and EtOAc

resulting in a Coulomb repulsion of the neighboring orbitals belonging to 3-ethylpyridinium and oxazole (Fig. 7). The twisted conformation of the emitting state of 1a is also supported by its moderate fluorescence quantum yield: the $\varphi_{\rm f}$ values of related ionic conformers, completely twisted to 90°, are below 0.01 [26]. In addition, the twisting process enhances the population in the excited state, reflected in larger emission bandwidth of 1a (Fig. 2a, Table 1). As shown above, the activation energies (E_a^{ET}) of intramolecular electron transfer for DMABN-related compounds in MeCN are 4.53–15.9 kJ /mole bigger than the corresponding E_{2}^{TICT} for the twisting of N(Me)₂ or N(Et)₂ groups [24]. Despite structural relaxation exhibiting a non-activated character, we suggest that the formation of a twisted conformer of 1a proceeds slower than the charge shift itself, within a ps time scale. This agrees with the data in a review [27] where, for various sorts of molecules, the solvation dynamics in aprotic solvents were much faster than the twisting reaction. Thus, the photorelaxation of **1a** proceeds via two channels: energy losses induced by the charge shift and structural relaxation (Scheme 2).

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Declarations

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

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