Early bird or night owl? Controlling the ultrafast photodynamics of triphenylamine substituted 2,2´:6´,2´´-terpyridine

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Controlling the ultrafast photodynamics of metal-free organic molecules has great potential for technological applications. In this work, we use solvent polarity and viscosity as “external knobs” to govern the photodynamics of an electron-donating derivative of 2,2′,6′,2′′-terpyridine (**terpy**), namely 4′-(4-(di(4-tert-butylphenyl)amine)phenyl)-2,2′,6′,2′′-terpyridine (**tBuTPAterpy**). We combine femtosecond fluorescence upconversion (FlUC) and transient absorption (TA) spectrocopies to provide a comprehensive description of the **tBuTPAterpy**’s photodynamics. Our results demonstrate that, by changing the solvent, the time scale of light-induced conformational changes of the system can be tuned over two orders of magnitudes, controlling the **tBuTPAterpy** fluorescence spectral region and yield. As a result, depending on the local environment, **tBuTPAterpy** can act either as an “early bird” or “night owl”, with a tunability that makes it a promising candidate for metal-free sensors.

Introduction

Intramolecular charge transfer (ICT) is a fundamental phenomenon responsible for a large number of chemical and biological processes in organic and inorganic systems [1]. Several investigations were devoted to ICT, which is exploited in applications for molecular electronics, solar energy-conversion, quantum optics and chemical sensors [2–7]. In addition, the fundamental understanding of ICT has fascinated scientists over the past decades [8–20]. In ICT systems, the early photodynamics upon optical transitions to the lowest electronic states is associated with the population transfer from the locally-excited (LE) Franck-Condon (FC) region to the relaxed geometry of the ICT state [21]. These conformational changes include twisting [9,22–27], planarization [23,24,27–30], bending [31], rehybridization of molecular fragments within the ICT moiety [13,32], and/or intersystem crossing (ISC) to the triplet manifold [33–37]. Such structural and electronic changes are strongly influenced by environment effects. As a consequence, solvent parameters like polarity and viscosity can be used as experimental knobs for the external control of the ICT photodynamics [3]. A rational design of ICT devices requires characterizing their ultrafast photodynamics and quantifying the impact of solvent parameters on their photoresponse [21].

Herein, we focus on the donor-acceptor molecule 4′-(4-(di(4-tert-butylphenyl)amine)phenyl)-2,2′,6′,2′′-terpyridine (**tBuTPAterpy**). Derivatives of 2,2′,6′,2′′-terpyridine (**terpy**) are among the most important organic ligands in coordination chemistry [38–46]. Several spectroscopic investigations described the photophysical properties of transition metal complexes with **terpy** ligands [43,46–51], showing that electron-donating substituents lengthen the photoluminescence lifetime of the compounds. This is generally due to an energy barrier increase between the emissive metal-to-ligand charge transfer triplet (^{3}MLCT) state and metal-centred triplet (^{3}MC) state [52–55], or to the equilibration between the ^{3}MLCT state and the intraligand triplet (^{3}ILCT/^{3}IL) state [47,51,56,57]. Despite the widespread use of **terpys** and their derivatives, the photophysics of the isolated ligands was to a great extent overlooked. Only a limited number of studies described the ultrafast photodynamic of these organic compounds [58,59], underestimating the great potential of these metal-free systems for applications.

In a recent study [60], we investigated the steady-state properties of **tBuTPAterpy,** showing that it is highly sensitive to solvent polarity, viscosity and pH. These features, together with its high fluorescence quantum yield (Φ_{PL} = 0.48 – 0.83 and τ_{PL} = 1.53 – 6.56 ns), make it a potential candidate as a metal-free environment sensor. Our previous joint experimental and computational work provided a picture of **tBuTPAterpy**’s energy diagram, showing that the absorption process is dominated by an ICT $S_0 \rightarrow S_1$ transition, while the near-lying $S_0 \rightarrow S_2$ transition has an oscillator strength several orders of magnitude lower. However, fully exploiting the applicative

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Electronic Supplementary Information (ESI) available: details about experiments, photodamage and fluence dependence tests, comparison of time-resolved spectra to steady state spectra, DAS and EAS, details about global fitting procedures. See DOI: 10.1039/x0xx00000x potentials of this system requires a better understanding of how the environment influences its early photodynamics, which governs its final emission properties. In this work, we performed a detailed study of the **tBuTPAterpy** ultrafast photoresponse using femtosecond fluorescence upconversion (FlUC) and femtosecond transient absorption (TA) spectroscopy, rationalizing solvent polarity and viscosity effects on the system's photophysics. In chloroform, we show that at least three conformers participate in the deactivation pathways of the molecule. Increasing the solvent polarity leads to a barrier-less motion that activates a conformational change to the lowest energy excited state on sub-ps time scales, while higher solvent viscosities slow down the process up to hundreds of ps. Finally, in absence of strong polarity and viscosity effects, the ISC to the triplet manifold becomes the dominant process.

Experimental

Materials.

tBuTPAterpy was obtained according to the procedure described in [51]. Analytical data for **tBuTPAterpy** (^{1}H and ^{13}C NMR spectroscopy and elemental analysis) are reported in the electronic supporting information (ESI), and are in good agreement with those discussed in ref. [51]. All solvents were of spectroscopic grade. They were commercially available and were used without further purification.

Measurement techniques, sample preparation and method of analysis.

FlUC and TA spectroscopy studies were conducted using the setups described in [61,62], and additional details are reported in the ESI. Quartz cuvettes of 2 mm (TA) and 1 mm (FlUC) thicknesses were used for sample solutions having concentrations of 125 µM and 250 µM, respectively. The stability of **tBuTPAterpy** in chloroform, acetonitrile, glycerol triacetate and *n*-hexane was spectrophotometrically monitored over 48 hours prior to the analysis (Figure S1, ESI). Photostability experiments and fluence dependence characterizations are reported in Figures S2-S3, respectively.

The FlUC setup consists of a Ti:sapphire laser (Libra, Coherent, 800 nm central wavelength, 45 fs pulses duration, 1 kHz repetition rate) and a FlUC spectrofluorimeter (LIOP- TEC). 400 nm excitation pulses were produced by doubling the 800 nm light with a I type BBO crystal (d = 0.5 mm). The sample solution was excited in the magic angle geometry (54.7°). The II sum-frequency generation was obtained from the horizontally polarized gate beam and the vertically polarized fluorescence. The upconverted light was collected with an unfolded Czerny-Turner spectrograph and detected with a CCD camera (Newton 920, Andor). The instrument response function (IRF) of the measurements was estimated from the full widths at half maximum (FWHM) of the cross-correlation signal of the pump and probe pulses, corresponding to 0.140 ps and 0.150 ps, respectively for $CHCl_3$ and acetonitrile solutions.

The TA spectra were measured using a Helios setup (Ultrafast Systems) equipped with a femtosecond Ti:sapphire regenerative amplified laser system (Astrella, Coherent, 800 nm central wavelength, 1 kHz repetition rate). A CaF_2 crystal and an optical parametric amplifier (Light Conversion, TOPAS prime) were used for the generation of the white light probe and the 405 nm pump beam, respectively. A CCD detector was used to collect the TA signal in transmission geometry. The IRF was measured in pure solvents (FWHM of about 160 fs, 150 fs, 150 fs, 150 fs were measured in $CHCl_3$, glyceryl triacetate, acetonitrile, *n*-hexane, respectively).

The Surface Xplorer (Ultrafast Systems) software was employed for the data processing of the TA data sets. The analysis of FlUC and TA data sets was performed using the Optimus™ software [63]. A detailed description of the data analysis procedure is given in the ESI.

Results and discussion

FlUC and TA of **tBuTPAterpy** were measured in both $CHCl_3$ (ε = 4.81, η = 0.51 cP) and acetonitrile (ε = 37.5, η = 0.34 cP), while TA data were further collected varying the solvent polarity and viscosity, respectively measuring the system in *n*-hexane (ε = 1.88, η = 0.28 cP), and glyceryl triacetate (triacetine, ε = 7.01, η = 25 cP). The results are summarized in Table 1, in Figure 1 (FlUC in $CHCl_3$) and in Figures 2 – 5 (TA in all solvents), and are discussed in more detail hereafter. Additional information is reported in Figures S4-S14 in the ESI.

Femtosecond studies in chloroform.

The FlUC results of **tBuTPAterpy** in $CHCl_3$ are shown in Figure 1 (see also Figures S4-S5 in ESI). Within the first 10 ps of the dynamics, the fluorescence signal grows and shifts towards lower energies and decays at longer time scales (Figures 1A-B). The emission band centred at ~21740 cm^{-1} (460 nm), which promptly appears after the pump pulse, largely overlaps with the steady-state emission spectrum of **tBuTPAterpy** at 77 K (see Figure S4, panel D). Instead, the band after 1000 ps time delay, which is centred at ~20410 cm^{-1} (490 nm), matches well the steady-state emission spectrum at room temperature (Figure S4, panel D). Time-resolved area normalized emission spectra (TRANES, Figure 1C) show a quasi-isoemissive point at ~21000 cm^{-1} (475 nm) for time delays longer than 10 ps, pointing to the presence of two transient emitting states [20,64–69].

To obtain further insights into the relaxation dynamics of **tBuTPAterpy**, a global lifetime analysis of the FlUC data was performed, with the best fit achieved using a four-component exponential decay model. Three-component fits were attempted without reaching a satisfactory agreement with the experiment, whereas adding a fifth component to the four-component fit did not provide significant improvements, as

Table 1. FlUC and TA decay lifetimes (ps) of **tBuTPAterpy** in the investigated solvents obtained from the global fit analysis.

	FlUC			TA			
	$CHCl_3$	CH_3CN		$CHCl_3$	CH_3CN	*n*-hexane	triacetine
τ_1	0.31	0.23	τ_1	0.54	0.20	–	0.67
τ_2	3.7	1.2	τ_2	3.1	1.4	–	10
τ_3	9.8	–	τ_3	8.9	–	–	110
τ_4	–	–	τ_4	210	110	72	560
τ_5	Infinite	Infinite	τ_5	4400	5800	1600	4800
τ_6	–	–	τ_6	–	–	Infinite	–

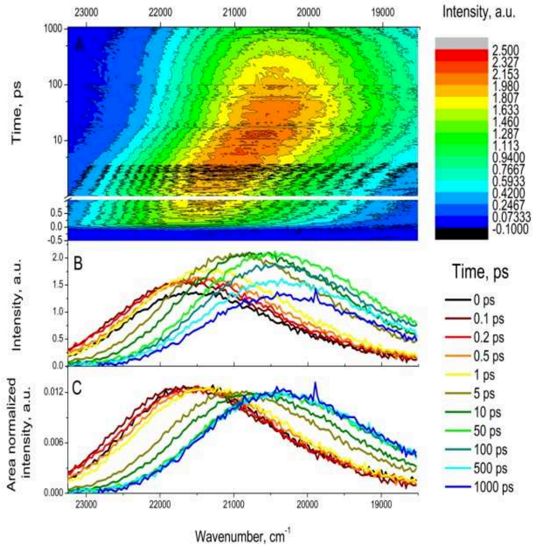

Figure 1. FlUC data for **tBuTPAterpy** in chloroform solution: 2D time-wavenumber plot (A); FlUC spectra at selected time delays (B); TRANES (C). The time axis break at 1 ps separates linear and logarithmic ranges.

shown in Figure S15 in the ESI. The two shortest components, τ_1 and τ_2, respectively of 0.31 ps and 3.7 ps, agree well with the inertial (0.285 ps) and diffusional (4.15 ps) solvation processes in chloroform for coumarin153 [70], while the longer time constants τ_3 and τ_4 are ascribed to solute kinetics. These results are complemented and confirmed by the TA measurements presented in the following.

Figure 2A shows the TA signal of **tBuTPAterpy** in $CHCl_3$. On sub-ps time scales, it consists of two negative and two positive alternating regions. The negative features correspond to a ground-state bleaching (GSB) in the energy range 28600 cm^{-1} – 25000 cm^{-1} (350 – 400 nm) and to a stimulated emission band (SE^1) lying between 22700 cm^{-1} (441 nm) and 20800 cm^{-1} (481 nm). The latter overlaps well the fluorescence spectra at short time scales of Figure 1. The two positive bands are related to excited state absorption (ESA) processes and lie at 25000 – 22700 cm^{-1} (400 – 441 nm, ESA^1) and 20800 – 16700 cm^{-1} (481 – 599 nm, ESA^2). Within 1 ps after excitation, a third band (ESA^3) appears between 16700 cm^{-1} (599 nm) and 14900 cm^{-1} (671 nm). The SE^1 band grows during the first 2 ps and red-shifts into a new band (SE^2) at longer time delays. The presence of an isoemissive point at 20890 cm^{-1} (479 nm) supports the assignment of these emission bands to two different transient species. The ESA^2 band grows within the IRF and starts decaying on sub-ps time scale. As reported for similar π-conjugate structures[58,59], we assign it to $S^1 \rightarrow S^n$ transitions within the **terpy** moiety. The narrow and intense ESA^1 band is typical of polypyridine anion radicals[71] in free organic ligands and their metal coordination compounds[72–75]. Instead, the ESA^3 band is ascribed to the cation radical species of the donor unit[76]. The coexistence of ESA^1 and ESA^3 transient signals respectively corresponding to anion and cation radicals is consistent with a photoinduced ICT process. The experimental results are satisfactorily reproduced using a five-component global target analysis (see Table 1, and also Figures S6 and S17 for a complete set of time traces and for the map of residuals). The obtained time constants are in good agreement with the FlUC analysis, with the notable exception for the presence of an additional time constant of 210 ps in the TA fit (Table 1). Based on the analysis of the TA spectra at different time delays, we conclude that:

(i) the GSB and all ESA features start growing within the IRF of the experiment;

(ii) the first component with a lifetime of τ_1=0.54 ps is related to the formation of SE^1, and a partial growth (decay) of ESA^1 (ESA^2). These signals reflect the formation of an S_1 excited state having a moderate ICT character and populating the lowest unoccupied molecular orbital (LUMO) centred on the **terpy** moiety [60]. At these time scales, the SE^1 band and the FlUC signal are blue-shifted with respect to the room temperature emission spectrum. As discussed in [60], this is typical of the **tBuTPAterpy** system in absence of structural changes with respect to the FC geometry;

(iii) the time constant τ_2 (3.1 ps) is associated with a progressive red shift and intensity drop of the SE^1 and ESA^2 bands, and a further growth of the ESA^1 band;

(iv) during τ_3 (8.9 ps), the ESA^1 band keeps growing, whereas the SE^1 band red shifts towards the newly formed SE^2 band, giving rise to the isoemissive point at 21050 cm^{-1} (475 nm). During τ_2 and τ_3, the system undergoes a relaxation process towards a molecular configuration having an emission spectrum compatible with room temperature fluorescence (see Figure S4, panel D). This observation, together with the presence of the ESA^1 and ESA^3 bands, is consistent with the formation of an ICT state upon conformational changes of the molecular moieties [60];

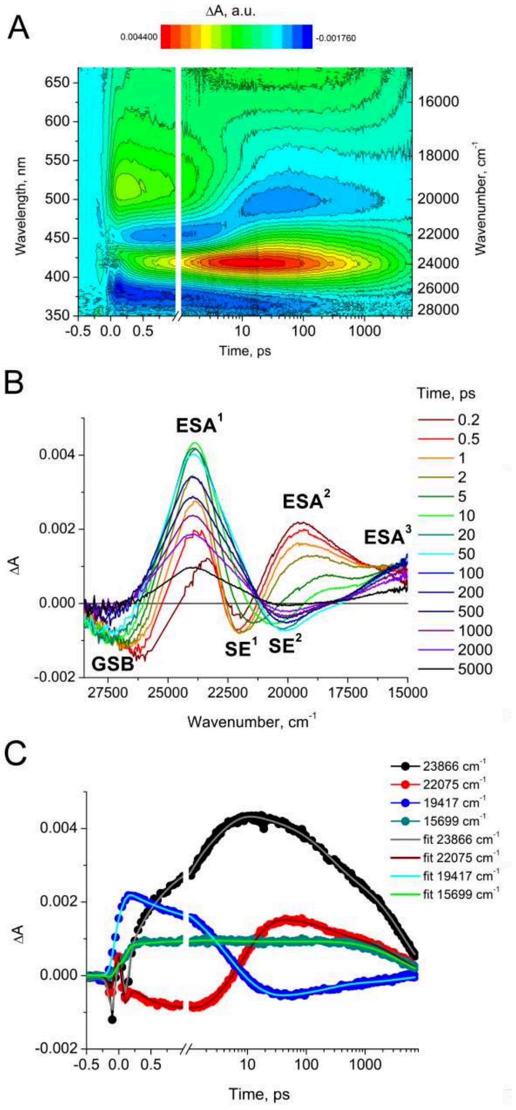

Figure 2. TA 2D maps (panel A), TA spectra at selected time delays (panel B), selected time traces with their fits (panel C) for **tBuTPAterpy** in CHCl$_3$. The time axis break at 1 ps separates linear and logarithmic ranges.

(v) the τ_4 time component (210 ps) is mostly associated with the decay of the ESA^1 and SE^2 features;

(vi) the τ_5 time constant of 4.4 ns agrees with the photoluminescence decay times measured in TCSPC (4.3 ns) and therefore corresponds to the radiative decay of the final excited state.

Figures S5 and S6 in ESI show the comparison of absorption, emission and excitation steady-state spectra of **tBuTPAterpy** in CHCl$_3$ with FlUC and TA energy traces at multiple time delays, and TA time traces with their fits, respectively.

Femtosecond studies in acetonitrile and n-hexane.

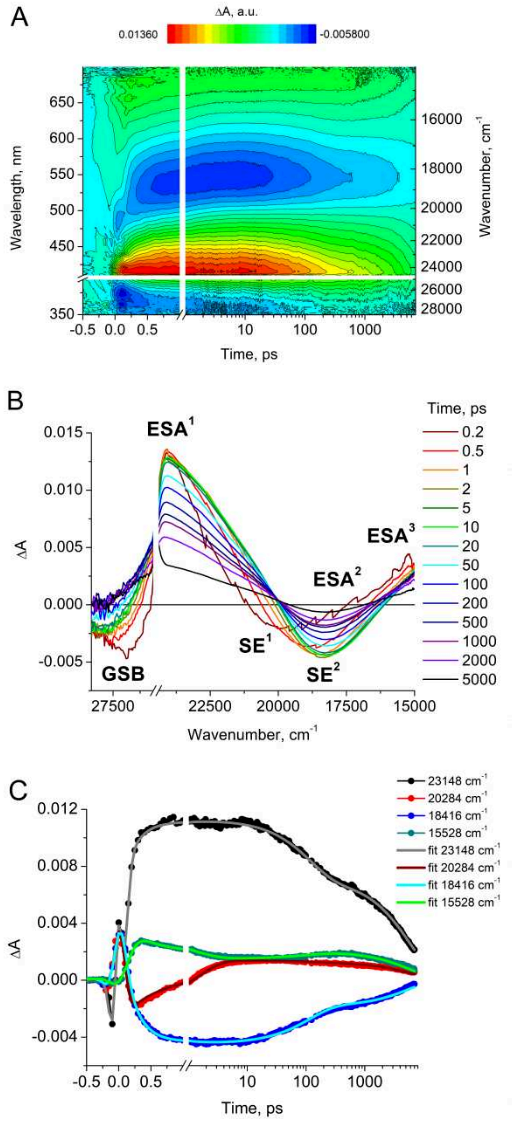

Figure 3. TA 2D maps (panel A), TA spectra at selected time delays (panel B), selected time traces with their fits (panel C) for **tBuTPAterpy** in acetonitrile. The time axis break at 1 ps separates linear and logarithmic ranges, whereas the axis break at 25316 - 24390 cm^{-1} (395 – 410 nm) corresponds to the photon energy of the Raman scattering of the acetonitrile solvent and was excluded from the analysis.

The comparison of TA experiments in solvents of higher (acetonitrile) and lower (*n*-hexane) polarity with respect to the moderately polar $CHCl_3$ provides a better understanding of how the solvent polarity affects the photodynamics of the push-pull **tBuTPAterpy** molecule (Figures 3 and 4).

In acetonitrile (Figure 3), the TA spectral shapes resemble those in chloroform, showing only a minor hypsochromic shift of the ESA^1 band and a bathochromic shift of the SE^2 band. However, differently from chloroform, the best fit of the TA global target analysis was achieved with a four-component model (see Figures S8 and S18). In this case, the spectral changes from the SE^1 to the SE^2 band occur almost immediately after photoexcitation, giving rise to an isoemissive point at 20040 cm^{-1} (499 nm) between the traces at 0.2 and 0.5 ps (Figure 3B). The τ_1 and τ_2 components approximately agree with the time constants previously reported for the solvation dynamics of coumarin153 in acetonitrile[70]. Thus, if a population transfer occurs between two different emitting states, it overlaps with the sub-ps inertial solvation process, explaining the absence of a fifth time component in the fit with respect to the chloroform data set. This observation agrees with the TRANES results of the FlUC measurements in acetonitrile , where no isoemissive point is observed (Figures S9) and where the transient spectral shifts are typical of solvation dynamics time scales. Similar to chloroform, in acetonitrile the TA fit of **tBuTPAterpy** requires one additional component (four) with respect to FlUC data (three), as reported in Table 1.

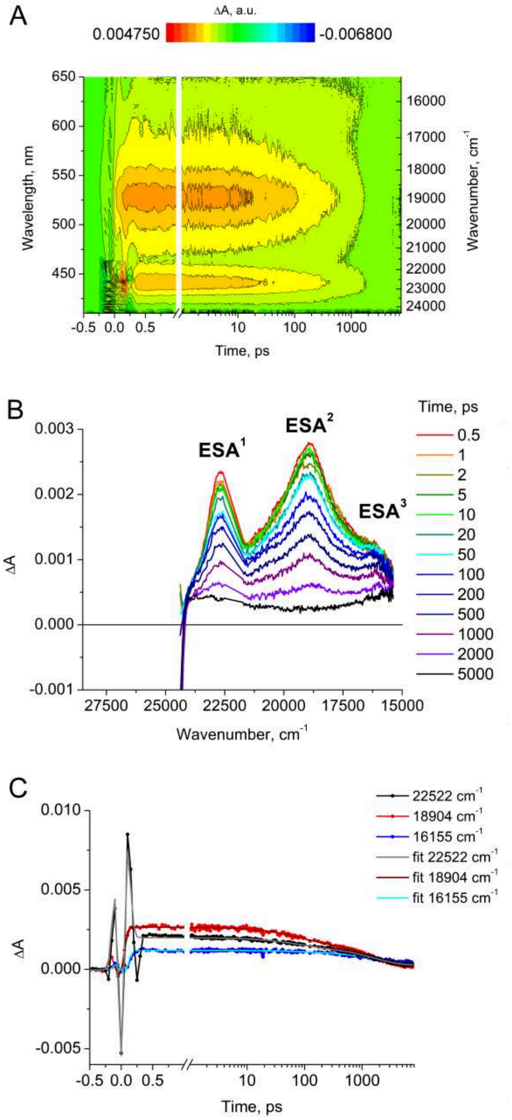

Figure 4. TA 2D maps (panel A), TA spectra at selected time delays (panel B), selected time traces with their fits (panel C) for **tBuTPAterpy** in *n*-hexane. The time axis break at 1 ps separates linear and logarithmic ranges.

In the non-polar *n*-hexane, the transient signal intensity is significantly lower than in the polar solvents under similar pump fluences. This is a consequence of the hypsochromic shift of the steady-state **tBuTPAterpy** absorption onset, which leads to a lower sample absorbance at 24690 cm^{-1} (405 nm). Compared to chloroform, both ESA^1 and ESA^2 bands are bathochromically shifted of about 500 – 1300 cm^{-1}, while a hypsochromic shift of ~950 cm^{-1} is observed in the case of ESA^3 band. The SE^1 band [60] is buried under the stronger ESA^1 signal, resulting in a positive feature of the TA map (see Figure S11 for the comparison of TA spectra with the steady-state spectra in *n*-hexane). The global lifetime analysis of the *n*-hexane data was performed using three components (see Table 1, Figure 4C, and Figures S12, which shows details of the global analysis in *n*-hexane). Both the first and second time constants correspond to a decay of the positive signal, with the latter closely resembling the PL decay time in *n*-hexane (1.53 ns). By comparing the results in *n*-hexane and $CHCl_3$, a remarkable difference is the presence of a persisting signal up to the longest measured delays in *n*-hexane. This “slow” component is characteristic of the ESA^1 and ESA^3 bands only, which have maxima respectively at 23810 cm^{-1} (420 nm) and <15400 cm^{-1} (>649 nm). Instead, the ESA^2 band disappears at about 5000 ps time delay. In the ns time delay range, the transients agree with the triplet-triplet ESA bands of the TA spectra of TPA-substituted benzimidazole derivatives, as reported in [37].

Femtosecond studies in glyceryl acetate.

The TA 2D map of **tBuTPAterpy** in the viscous triacetine solvent is reported in Figure 5 (panel A). The spectral profiles resemble the TA spectra in $CHCl_3$: the ESA bands are in the same energy range, and the SE^1 and SE^2 bands undergo similar spectral changes. The position of the SE^2 band agrees with the steady-state emission spectrum of **tBuTPAterpy** in the triacetine solvent (see Figure S13 in ESI), and the 2D map is satisfactorily fitted using a five-component model. However, with respect to $CHCl_3$ the system’s photodynamics significantly slows down upon increase of the solvent viscosity (see Table 1 and Figures S14, S20 in the ESI for details about the global analysis). The highest increase concerns τ_3, which is one order of magnitude larger in triacetine than in chloroform, suggesting that this time constant corresponds to a conformational change of the solute. The isoemissive point at 20880 cm^{-1} (479 nm) further suggests the presence of two

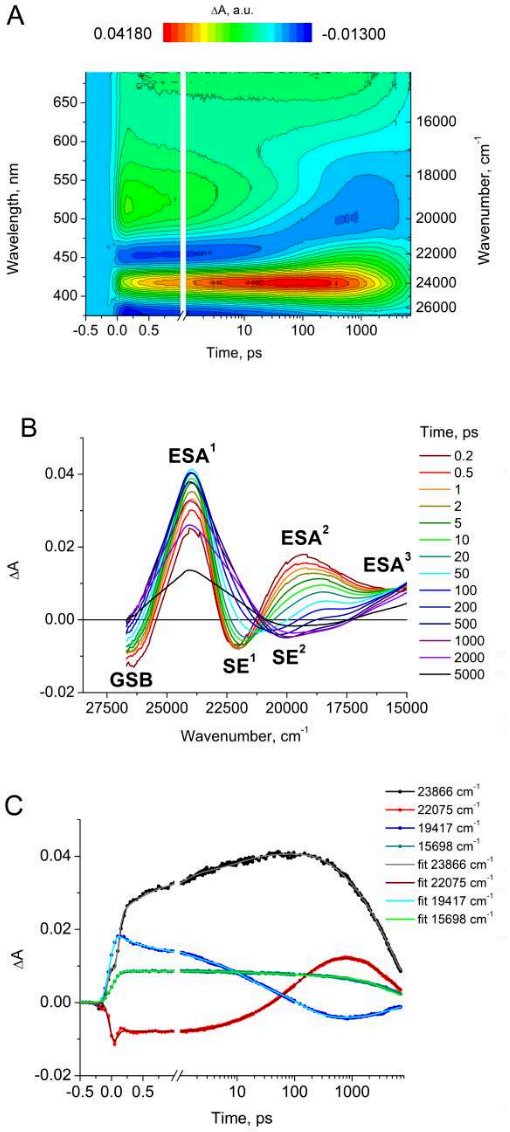

Figure 5. TA 2D maps (panel A), TA spectra at selected time delays (panel B), selected time traces with their fits (panel C) for **tBuTPAterpy** in glyceryl acetate. The time axis break at 1 ps separates linear and logarithmic ranges.

emissive states. Instead, the τ_5 component matches the decay time observed in the TCSPC measurement [60]. Minor differences between the two solvents are also present, as the absence of an initial blue shift of the ESA^1 band and a fast growth of the SE^1 band within τ_1 (not within τ_2, as it happens in chloroform).

Excited state kinetics of tBuTPAterpy.

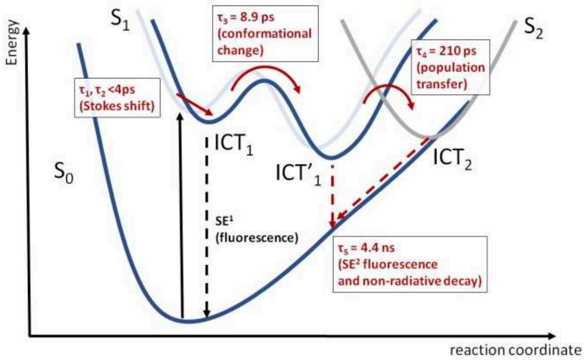

Figure 6. Schematic of the excited state dynamics of tBuTPAterpy in CHCl$_3$.

The proposed energy diagram for **tBuTPAterpy** in CHCl$_3$ is shown in Figure 6. The excitation at 405 nm populates the short-lived excited state S$_1$, which has a moderate intramolecular charge transfer character (ICT$_1$), as reported in [60]. The inertial and diffusive solvation processes, which are responsible for the first two-time components of the photodynamics, stabilize the ICT$_1$ state, leading to a Stokes shift of the emissive band.

The third relaxation process, which is strongly affected by the solvent viscosity (see triacetine results), is ascribed to a conformational change towards a new, lower in energy, charge-transfer state (ICT´$_1$). Such a population transfer between two different excited-state conformers is consistent with the presence of an isoemissive point in both TRANES and SE bands. The ICT´$_1$ state is responsible for the steady-state fluorescence of **tBuTPAterpy**, as confirmed by the overlap of the late FlUC transient emission spectrum and the room temperature emission signal of the system (see Figure S4). Furthermore, the ICT´$_1$ emission decays in few ns, in agreement with the time scales observed in the TCSPC experiment [60].

The second to last time constant, which is present in the TA experiments but not in the FlUC data set, suggests the existence of a small fraction of photoexcited **tBuTPAterpy** in a non-radiative state (ICT$_2$), which might be populated alternatively to the ICT´$_1$ conformer. We ascribe the ICT$_2$ conformer to the S$_2$ “dark” state reported in [60], which has an ICT character and almost zero transition moment due to the marginal overlap of the π-conjugated orbitals involved in the electronic transition to the ground state. Since this state is non-emissive and is not observed in the FlUC experiment, we interpret the 210 ps (560 ps) decay component of **tBuTPAterpy** in CHCl$_3$ (triacetine) as a population transfer from ICT´$_1$ to ICT$_2$, which further decays to the ground state *via* a conical intersection.

Changing the solvent leads to modifications of the early photodynamics of **tBuTPAterpy**, e.g., the rate of conformational change of the system can be modulated by changing the viscosity while keeping the same polarity. Hence, in the viscous triacetine we observe a lengthening of the time components ascribed to population transfer between the ICT$_1$ and ICT´$_1$ conformers, and between the ICT´$_1$ and ICT$_2$ states.

Instead, more polar environments facilitate the formation of the ICT´$_1$ state, stabilizing it and lowering the conformational energy barrier with the initially populated ICT$_1$ state, similarly to what was reported for push-pull pyridium salts by Carlotti et al [77]. Thus, in the highly polar acetonitrile, the **tBuTPAterpy** photodynamics is solvation-controlled, while in the moderately polar CHCl$_3$ it is controlled by the slower conformational changes.

Finally, since pronounced solvent polarity is required for the stabilization of the CT states, the apolar n-hexane favours a different relaxation pathway over the $ICT_1 \rightarrow ICT'_1$ population transfer, namely an ISC process to the triplet manifold. The ICT_1 (S_1) → LE (T_n) process, which is allowed by the El-Sayed rule, was previously observed in apolar solvents in the case of 2,6-bis(diphenylamino)anthraquinone [36]. In the specific case of the push-pull **tBuTPAterpy** system, the population of the initially formed ICT_1 (S_1) state is directly transferred to the LE (T_1) triplet state localized on the 4-(di(4-tert-butylphenyl)amine)phenyl moiety before the structural change to the ICT'_1 conformer occurs, a process which is possibly slowed down by a high conformational energy barrier.

Conclusions

In this work we characterized the ultrafast photodynamics of the push-pull molecule **tBuTPAterpy**, rationalizing the solvent polarity- and viscosity-dependence of its steady-state properties that we analysed in our previous study [60]. Based on FlUC and TA measurements as a function of solvent properties, we proposed a diagram describing the system's relaxation dynamics in $CHCl_3$, showing the presence of multiple transient ICT conformers. Upon photoexcitation, **tBuTPAterpy** populates an ICT state (ICT_1) which undergoes energy stabilization due to solvent relaxation processes. Within 10 ps, a structural change leads to a population transfer to a second emitting conformer, ICT'_1, which decays to the ground state through a fluorescence channel occurring in the ns time scales. We also determined the presence of a second "dark" ICT conformer (ICT_2), populated on longer time scales (~200 ps) and undergoing non-radiative decay to the ground state.

By combining ultrafast measurements as a function of solvent polarity and viscosity, we confirmed the interpretation proposed in the energy diagram and explained how the environment influences the **tBuTPAterpy** photodynamics. Specifically, increasing the solvent viscosity slows down the $ICT_1 \rightarrow ICT'_1$ conformational change of about one order of magnitude, as observed in **tBuTPAterpy** in glyceryl triacetate. Conversely, a solvent polarity increase reduces the energy barrier of the $ICT_1 \rightarrow ICT'_1$ conformational change, speeding up a population transfer process which occurs on sub-ps time scales in acetonitrile. Instead, by minimizing the solvent polarity effects, as in the case of apolar *n*-hexane, a parallel pathway involving ISC is favoured. In this solvent, the ICT_1 (S_1) → LE (T_n) decay is the dominant relaxation channel and it occurs on shorter time scales than the conformational change. This observation can help the discovery of similar systems exhibiting thermally activated delayed fluorescence (TADF).

Overall, this study reveals the complexity of **tBuTPAterpy** photodynamic as a representative example of push-pull derivatives of 2,2′,6′,2′′-terpyridine. Even though these ligands are mostly used as building blocks in coordination chemistry for the enhancement of photoluminescence yields in metal complexes, our work stresses the potential of **terpy** derivatives as metal-free environment probes whose photodynamics can be easily controlled through external solvent parameters. The reported ultrafast investigation confirms that **tBuTPAterpy** is a promising candidate for sensing applications and it provides a fundamental understanding of its excited state dynamics, laying the foundations for chemical and technological optimisations of metal-free sensors.

Author Contributions

Conceptualisation, A.M.M., O.C. and M.C.; methodology, A.M.M., O.C. and M.O.; software, A.M.M; validation, A.M.M., O.C. and B.M.; formal analysis, A.M.M., O.C. and E.C.S.; investigation, A.M.M. and E.C.S.; resources, A.M.M., B.M. and M.C.; data curation, A.M.M., O.C. and E.C.S.; writing—original draft preparation, A.M.M., O.C. and B.M.; writing—review and editing, A.M.M., O.C., M.O., B.M. and M.C.; visualisation, A.M.M., O.C. and M.C.; supervision, A.M.M. and M.C.; project administration, A.M.M.; funding acquisition, A.M.M, B.M. and M.C. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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