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Ultrafast Processes in Upper Excited Singlet States of Free and Caged 7-Diethylaminothiocoumarin

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Abstract

The photochemistry and photophysics of thiocarbonyl compounds, analogues of carbonyl compounds with sulfur, have long been overshadowed by their counterparts. However, recent interest in visible light reactions has reignited attention towards these compounds due to their unique excited state properties. This study delves into the ultrafast dynamics of 7-diethylaminothiocoumarin (TC1), a close analogue of a well-known probe molecule coumarin 1 (C1), to estimate intersystem crossing rates, understand the mechanism of fluorescence and phosphorescence, and evaluate TC1's potential as a solvation dynamics probe. Enclosing TC1 within an organic capsule indicates its potential applications even in aqueous environments. Ultrafast studies reveal a dominant sub-picosecond intersystem crossing process, indicating the importance of upper excited singlet and triplet states in the molecule's photochemistry. The distinct fluorescence and phosphorescence origins, along with the presence of closely spaced singlet excited states, support the observed efficient intersystem crossing. The sulfur atom alters the excited state behavior, shedding light on reactive triplet states and paving the way for further investigations.

Introduction

The photochemistry and photophysics of thiocarbonyl compunds, i.e. the sulfur analogues of carbonyl compounds, have been overlooked for decades in favor of carbonyl compounds.[1-4] Despite the undesirable characteristics such as foul smell and poor stability, these molecules have been established to possess interesting excited state properties such as emission[5] and reactivity from upper excited states[3] and quantitative rapid conversion to lower triplet from excited singlet manifold.[6] Fortunately, smell is compensated by attractive color of these molecules. Recent interest in conducting reactions with visible light, has refocussed the attention on molecules containing thiocarbonyl chromophore.[7-10]

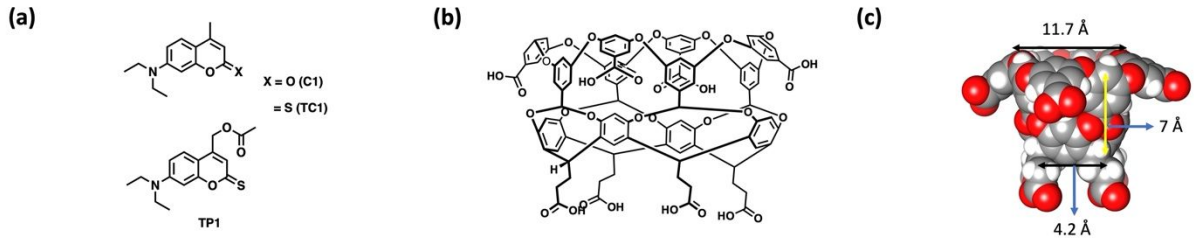
One of the current authors' interest in thiocarbonyl compounds dates back to early 1970s.[11-13] Towards the waning years of his activities in this area, his group noted that thiocoumarins possess close to unity quantum yield of intersystem crossing (ISC) as well as several properties similar to diaryl, dialkyl and arylalkyl thioketones.[14-16] Unfortunately, unlike in thioketones, since S_2 and S_1 states are closer in energy in thiocoumarin it was not possible to identify reactions from upper excited states and unequivocally identify the electronic nature of the state from which the weak fluorescence and strong phosphorescence originate.[17] At that time, due to lack of ultrafast facilities, the rate and the origin of ISC could not be determined. In this article we have fulfilled the gap by probing the ultrafast dynamics of 7-diethylaminothiocoumarin (TC1, Scheme 1 for structure), a close analogue 7-diethylaminocoumarin (C1, Scheme 1). Our interest in TC1, as opposed to the parent thiocoumarin, derives from the central role of the analogous C1 in molecular photochemistry and photophysics. C1 is a well-known probe to monitor solvation dynamics in various media[18-24] and derivatives of it have served as photoprotecting groups in organic photochemistry.[25-28] We hoped that TC1 will display similar properties and thought therefore it is important to gain knowledge of its photophysics. Our goals in the current undertaking were to estimate the rates of ISC from the singlet manifold to the triplet, to understand the mechanism of ISC, to identify the origin of fluorescence and phosphorescence and to establish the viability of using TC1 as a probe to monitor solvation dynamics.

It is well known that the excited molecules possessing thiocarbonyl chromophore are deactivated through physical[29] and chemical quenching by self, solvent and oxygen.[1, 3, 12, 30-40] To isolate the molecule from the above solvent surroundings, another molecule of its own kind and oxygen, the excited state dynamics of a single TC1 molecule enclosed within an organic

capsule formed by two molecules of octa acid (Scheme 1) was investigated.[41-45] As expected, the dynamics were cleaner than in organic solvents and intense phosphorescene was recorded even at room temperature indicating that the TC1 molecule even in millisecond time scale was not exposed to exterior water molecules and oxygen.[46] As discussed below, the excited singlets live only for subpicsecond and in that time scale, certainly, the encaged TC1 is not expected to interact with any other molecules except the walls of the capsule. Thus, we were able to monitor the dynamics of an encaged TC1 molecule in aqueous solution at room temperature.

There have been a few ultrafast studies on thiocarbonyl molecules including parent thiocoumarin (TC).[47-51] A short S_2 lifetime of 100 fs[47] was reported in TC, being attributed to the presence of a conical intersection between S_2 to S_1. ISC is suggested to occur from S_1 to T_1. A series of indepth ultrafast studies on thiocarbonyl substituted nucleic acid bases reveal that the S_2 state of these molecules live only for a few hundreds of fs.[49-51] Once again, the short lifetime of S_2 is attributed to the presence of a conical intersection leading S_2 to S_1. The ISC to T_2 and T_1 is proposed to occur from S_1. Direct crossing from S_2 to the triplet manifold is suggested to be only a minor pathway. However, an early study suggested direct T_2 formation from S_2 of dialkyl thioketones.[52] The rapid ISC in these systems is suggested to involve crossing from S_2 to T_2 followed by internal conversion to T_1. Interestingly, even photoreactions are speculated to originate from T_2.[13, 53] Thus, in addition to S_1 and T_1, upper excited singlet and triplet states could play a role in the photochemistry and photophysics of TC1. The extraordinary short lifetimes and high triplet yields reported for thiocarbonyl substituted nucleic acid bases and various thioketones, prompted us to undertake a detailed ultrafast studies on TC1.

It is well-known that thiocarbonyls react with solvents from upper excited states and deactivate by interacting with solvent C-H bonds.[29, 37-38, 54-55] These make the study in organic solvents as well as OA encaged TC1 challenging, We believe the insights we gain from the current study with TC1 would help us exploit systems like TP1 (Scheme 1) as a photoprotecting group.[26] Surprisingly, we found that the absorption and excitation spectra for fluorescence in TC1 do not overlap suggesting that there is a hidden state with almost negligible absorption co-efficient.[56] Furthermore, we have made progress in identifying the states involved in the singlet-triplet crossing and measured the corresponding rates. However, the mechanistic origin of the fast ISC remains to be determined.



Scheme 1: (a) Molecular structure of 7-diethylaminocoumarin (coumarin-1 or C1), 7-diethylaminothiocoumarin (thiocoumarin-1 or TC1) and 7-diethylaminothiocoumarin phototrigger (TP1) (b) Chemical structure of water-soluble octa acid (OA) cavitand (c) Three-dimensional structure of OA cavitand.

Experimental Section

Materials

The synthesis and characterization of 7-diethylaminothiocoumarin (abbreviated as thiocoumarin-1 or TC1) are described in Scheme S1 of the SI. Coumarin-1 (Exciton Inc., USA) was used as received. All the solvents used in this work are of HPLC grade and purchased from Fischer Scientific, India. Octa acid (OA) was synthesized, purified, and characterized according to the reported procedure. [41]

Methods

Steady-state and time-resolved absorption/fluorescence studies: Steady-state absorption and emission spectra were recorded in a commercial UV-vis spectrophotometer (UV-2450, Shimadzu, Japan) and spectrofluorimeter (FluoroMax-4, Jobin-Yvon, USA), respectively, using 10 mm path length cuvette. The concentration of the sample was maintained close to 5 μM. Steady-state and time resolved fluorescence measurements at low temperature (77 K) were performed on FLS1000 spectrometer (Edinburgh Instruments, UK) employing quartz dewar filled with liquid nitrogen.

Femtosecond time-resolved fluorescence data was collected through fluorescence up-conversion method on a commercial setup (FOG-100, CDP Corp., Russia). The details of the setup can be found in our previous publications.[57] Briefly, the sample was excited at 400 nm using the second harmonic of a mode-locked Ti-sapphire laser (MaiTai-HP, Spectra Physics, USA). To generate second harmonic we used a 0.2 mm BBO crystal ($\theta = 25°$, $\varphi = 90°$). The fluorescence emitted from the sample was collected under the magic angle configuration and

was up-converted in another nonlinear crystal (0.2 mm BBO, $\Theta = 38°$, $\varphi = 90°$) using the fundamental beam as the gate pulse. The up-converted light is dispersed in a monochromator and detected by a photomultiplier tube. The femtosecond fluorescence decays were deconvoluted using a Gaussian shape for the instrument response function having a FWHM of 300 fs using commercial software (IGOR Pro, WaveMetrics, USA). The measurements were performed in a 1 mm path length rotating cell and the pump power was approximately ~13 mW.

Femtosecond transient absorption data were acquired on a commercial transient absorption spectrometer (FemtoFrame-II, IB Photonics, Bulgaria). The details of the setup are described earlier[58] and only a brief overview is presented here. The fundamental beam (800 nm, 80 fs, 3.7 mJ, 1 kHz) light was obtained from a Ti-Sapphire regenerative amplifier (Spitfire Pro XP, Spectra-Physics, USA) pumped by a 20 W Q-switched Nd:YLF laser (Empower, Spectra-Physics, USA) and seeded with a Ti-Sapphire femtosecond oscillator (MaiTai-SP, Spectra-Physics, USA). The fundamental light was divided into two parts. One part was passed through a BBO crystal to generate the 400 nm pump pulse while the other part of the beam was passed through a delay stage and focused on a sapphire crystal to generate the white light continuum that used as the probe light. After passing through the sample the probe light was dispersed in a polychromator and detected using a CCD detector. The power of the pump light was kept ~10 μW. The instrument response function was measured to be 150 fs.

Theoretical calculations. Density functional theory (DFT) calculations for TC1 were performed with Gaussian 16 package.[59] We employed the B3LYP[60] exchange-correlation functional along with the 6-31+G(d,p) basis set for C, H, N, O, and S in the ground state (S_0) optimization. Vertical transition energies from the ground electronic state (S_0) to higher electronic states were obtained by employing time-dependent DFT method (TDDFT) at B3LYP/6-31+G(d,p) level of theory. Solvation effects were modeled in the polarizable continuum model (PCM) with state-specific corrections according to the corrected linear-response (cLR-PCM) method by Caricato *et al.*[61]

Results and Discussion

Our initial studies revealed the fluorescence quantum yield (ϕ_f) of TC1 to be exceptionally low (~10^{-4}) compared to its oxygen analog C1 (0.73).[62] Further, the ϕ_f of TC1 was found to

depend strongly on the solvent (see Table S1 of the SI). In addition, the excitation spectrum of the fluorescence did not fully match with the absorption. These unusual observations prompted us to undertake ultrafast experiments whose results are discussed below.

Steady-state and time-resolved absorption/emission studies in solution. The steady-state absorption and emission spectra of TC1 in various polar and nonpolar solvents are shown in Figures 1a and 1b. In acetonitrile the absorption maximum is at 456 nm with the molar absorption coefficient (ε) of 43,500±750 M^{-1} cm^{-1} (see Figure S1). This is about two times higher than for C1.[63] Upon decreasing the polarity of the solvent a hypsochromic shifts of the absorption (left panel) and the emission (right panel) maxima are observed (see Table S1 of the SI for the data) suggesting the excited state dipole moment of TC1 to be higher than that of the ground state.

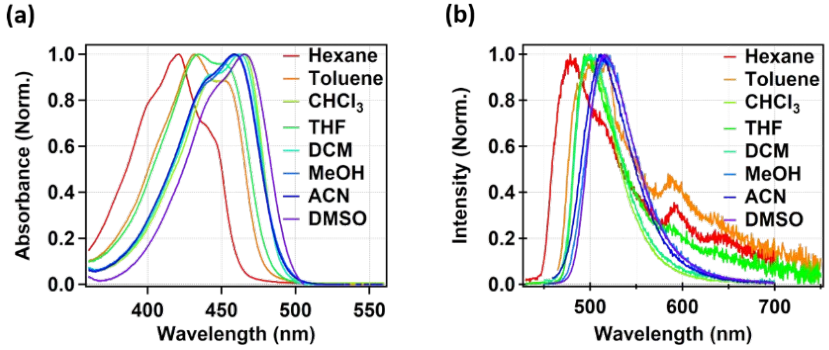


Figure 1. Steady-state (a) absorption and (b) emission spectra of TC1 in different solvents; hexane (λ_{ex} = 400 nm), toluene (λ_{ex} = 450 nm), chloroform (λ_{ex} = 440 nm), THF (λ_{ex} = 400 nm), DCM (λ_{ex} = 440 nm), MeOH (λ_{ex} = 440 nm), ACN (λ_{ex} = 440 nm), and DMSO (λ_{ex} = 440 nm) at 25°C All the absorption/emission measurements were done in aerated condition without any special treatment.

In nonpolar solvents (e.g. hexane, tetrahydrofuran and toluene), the major emission band near 500 nm is accompanied by two low intensity bands at 595 nm and 640 nm. In line with the previous works on thio-analogs of cyclic thioketones and thiocoumarins, we attribute these bands to phosphorescence.[1, 4, 46, 64] Emission recorded under oxygen and nitrogen saturated conditions (Figure 2a) confirmed the long wavelength emission to be phosphorescence. The emission with maxima at 595 and 640 nm that was weak under aerated conditions was completely quenched upon bubbling the solution with oxygen. However, saturation of the

solution with nitrogen brought back the emission. This observation leads us to conclude the origin of the 595 nm and 640 nm bands to be the triplet state. This observation is quite interesting as it established that thio-coumarin compounds are potential room temperature phosphorescence (RTP) molecules and might have wide applicability. A similar observation is also observed for TC1 in acetonitrile (see Figure S2 of the SI). To further confirm the origin, the emission spectra at 77 K in ethanol (polar) and methylcyclohexane (non-polar) glasses were recorded. From the spectra shown in Figures S3a-b (SI) we note an increase in intensities of the 595 nm and 640 nm bands upon lowering the temperature. This is due to suppression of oxygen and self quenching in a rigid glassy medium, phenomena well-established for thiocarbonyl systems in solution.[1, 3] The gated emission spectrum after 0.1 ms of the excitation, shown in Figure 2b, contains only bands above 580 nm. The emission decay monitored at 595 nm could be fitted to a single exponential function with a lifetime of 4.2 ms (Figure 2c). The long lifetime, intense emission at 77 K and oxygen quenching in solution support our conclusion that the long wavelength emission in non-polar solvents at room temperature is phosphorescence.

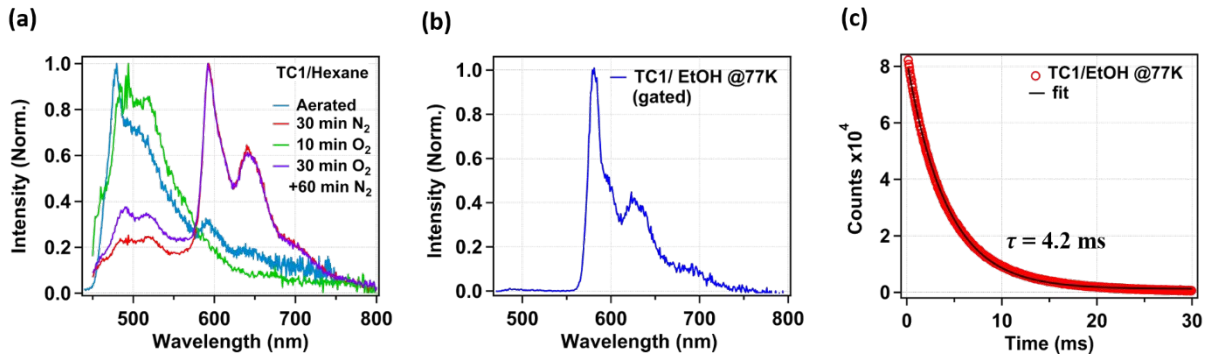


Figure 2. Steady-state emission in O_2/N_2 purged condition, time-gated emission spectroscopy and lifetime measurement: (a) Steady-state emission of TC1 in hexane in aerated and different purged conditions (b) Time-gated emission spectra ($\lambda_{ex} =$ 445 nm, delay 0.1 ms, gate width 3 ms) in EtOH glass a 77 K (c) Emission lifetime decay at 595 nm of TC1 in EtOH glass at 77 K.

To understand the origin of the fluorescence, the excitation spectra of TC1 in both polar and non-polar solvents were recorded and these with the absorption spectra are presented in Figures 3a-b and Figure S4 of the SI. Surprisingly, the excitation spectrum of TC1 is red-

shifted to absorption spectra both in hexane and acetonitrile. For C1 the excitation spectrum matches exactly with the absorption spectrum, which signifies that the emissive state is coupled with the Franck-Condon state (see Figure S5 of the SI). Earlier photophysical studies on parent thiocoumarin molecules reported the exact matching of excitation spectrum with the absorption spectrum.[48] However, as seen in Figure 3b, in TC1 the excitation spectrum does not match with the absorption spectrum, and this led us to conclude that the emissive state is not coupled to the FC state of the molecule.

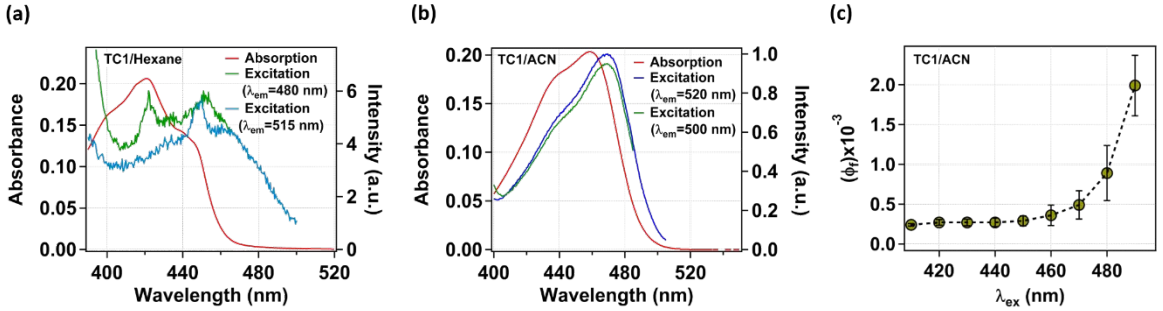


Figure 3. Steady-state excitation spectral measurement and fluorescence quantum yield measurement: Excitation spectra (right axis) and absorption spectra (left axis) of TC1 in (a) hexane (Hex) and (b) acetonitrile (ACN) in aerated condition at 25°C (λ_{em} for excitation spectral measurements are indicated in the figures). (c) Excitation wavelength-dependent fluorescence quantum yield of TC1 in ACN solvent in aerated condition at 25°C (Using the reference quantum yield 0.032 of coumarin 481 in 50 % ethanol).

To probe the origin of the unusual shift in the fluorescence excitation spectrum, we measured the excitation wavelength dependent fluorescence quantum yield (ϕ_f) (Figure 3c). According to Vavilov's rule, ϕ_f should be independent of the excitation wavelength for molecules emitting from the lowest excited singlet state, which is valid for most fluorophores. However, for TC1 in acetonitrile, we observed a 7-fold increase in ϕ_f upon changing the excitation wavelength from 440 nm ($\phi_f = 2.7 \times 10^{-4}$) to 490 nm ($\phi_f = 19.9 \times 10^{-4}$) (see Table S2 for measured data). This observation indicates the presence of a highly fluorescent low energy state that is feebly accessible by direct light absorption. We believe, the red-shifted state is strongly emissive, but has very low absorption cross-section. We propose that the measured absorption spectrum is a linear combination of the two lowest singlet excited states. Two orders lower ϕ_f in TC1 with respect to C1 is likely to be the result of the presence of faster non-radiative channels in the singlet manifold.

The fluorescence lifetime of TC1 in hexane, acetonitrile and dichloromethane at their corresponding emission maxima is measured using femtosecond fluorescence up-conversion technique; decay traces are displayed in Figure 4. In hexane, the lifetime of TC1 is found to be single expotential with a time constant of 150 fs. In the case of acetonitrile, the decay was best fitted to a biexponential function with two time constants of 1.2 ps (43%) and 4.7 ps (57%). The fluorescene decay time contstants of TC1 in hexane, acetonitrile, dichloromethane are tabulated in Table S3 of the SI. The fluorescence decay of TC1 in dichloromethane shows a bi-exponential behavior, like in acetonitrile. The origin of two lifetime components in acetonitrile and dichloromethane is proposed to be two closely spaced excited singlet states. If it is true, then we must expect a change in the excitation spectrum if the emission is monitored at different wavelengths. However, we have not seen any spectral shift of the excitation spectrum by changing the observed emission wavelength in acetonitrile and dichloromethane (see Figure 3b and Figure S6a of the SI). This is probably due to the large difference in the fluorescence quantum yield of the two emissive states in TC1. Quite likely the one with the larger quantum yield contributes to the overall emission. Earlier reports on parent thiocoumarin (TC) attributed the biexponential fluorescence decay to the equilibrated and unequilibrated vibrational energy levels of the singlet excited state.[48] If this is true, then we would expect a gradual shift in the emission spectra upon changing the excitation wavelength as was reported for TC. However, in this study, we have not seen any gradual shift of the emission maxima of TC1 in acetonitrile on changing the excitation wavelength (see Figure S6b of the SI). Rather, we observed a negligible shift in the emission maximum beyond a certain excitation wavelength (see Figure S6b of the SI). This indicates that the two emissive states of TC1 are not due to different vibrational levels within a single excited singlet manifold. In the case of TC1, in all likelihood, atleast two distinct electronic states play a role in this unusual phenomenon. Consistent with this, as discussed above, two lifetimes were measured in acetonitrile and dichloromethane. Most likely in the case of hexane, the limited time resolution of our instrument (IRF~250 fs) missed the second component.

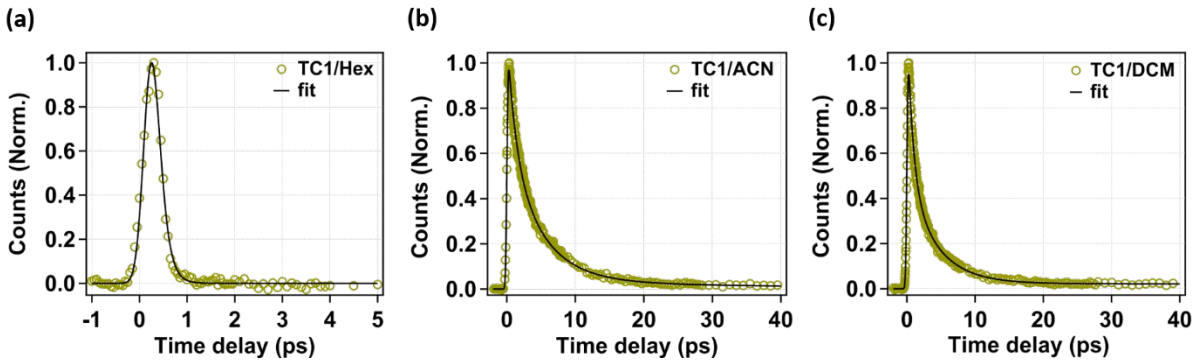


Figure 4. Fluorescence lifetime decays of TC1 in (a) hexane (Hex) (λ_{em} = 490 nm); (b) acetonitrile (ACN) (λ_{em} = 520 nm), and (c) dichloromethane (DCM) (λ_{em} = 510 nm) at 25 °C. All the fluorescence decays were measured in aerated condition.

The combined fluorescence quantum yield and lifetime data suggest that most of the excited state population in TC1 is dispersed through non-radiative pathways. Occurence of intense phosphorescence in low-temperature glass,[46] suggests that ISC is the most probable non-radiative channel operating in the excited singlet manifold of TC1. To authenticate this proposal, femtosecond transient absorption study was conducted. Transient absorption spectra of TC1 in hexane and acetonitrile at different probe delay times are presented in Figure 5. At very early times, a negative band appears that matches the steady-state emission spectrum (see Figure S7a,b of the SI), which is assigned to the stimulated emission (SE) band. This negative band converted to a broad positive band within a few picoseconds, that partially decays (until ~80-90 ps in both hexane and acetonitrile) and then remain unaltered till 1 ns (time window of our measurement). The positive band (460 nm to 730 nm) is assigned to the excited state absorption (ESA) band of the triplet state. The spectral feature of the ESA band in the early time (2 ps and 10 ps in the case of hexane and acetonitrile, respectively) found to be different compared to the same in the later time regime. The former has been assigned to the ESA of higher order triplet (T_n), whereas, the ESA band at the later time is assigned to the (T_1) state. Radiationless decay of T_n to T_1 is a spin allowed process, observation of a fast decay of the T_n state is not surprising. Similar transient spectral characteristics of TC1 have been found in dichloromethane (see Figures S8a of the SI). Thus, we believe the excited singlet decays to upper triplet that relaxes to T_1.

To get an idea about the time scale of triplet formation, we performed the kinetic analysis of the transient spectra (see Figures 5b,e and Table S4 of the SI). In hexane, we observed a rise time of 220 fs, which closely matches with the fluorescence lifetime of TC1. This observation indicates an ultrafast ISC for TC1 in hexane. The existance of the second emissive state of TC1 could not be resolved in hexane due to the limited time resolution of the instrument. On the other hand, in case of TC1 in acetonitrile, we observed two distinct rise time components (~500 fs and ~2 ps). Interestingly, during the lifetime measurement of TC1 in acetonitrile, we observed two decay time constants. A similar kinetic feature was observed in dichloromethane (see figures S8b of the SI). This is what we expected from our proposition of the existence of two emissive states in TC1.

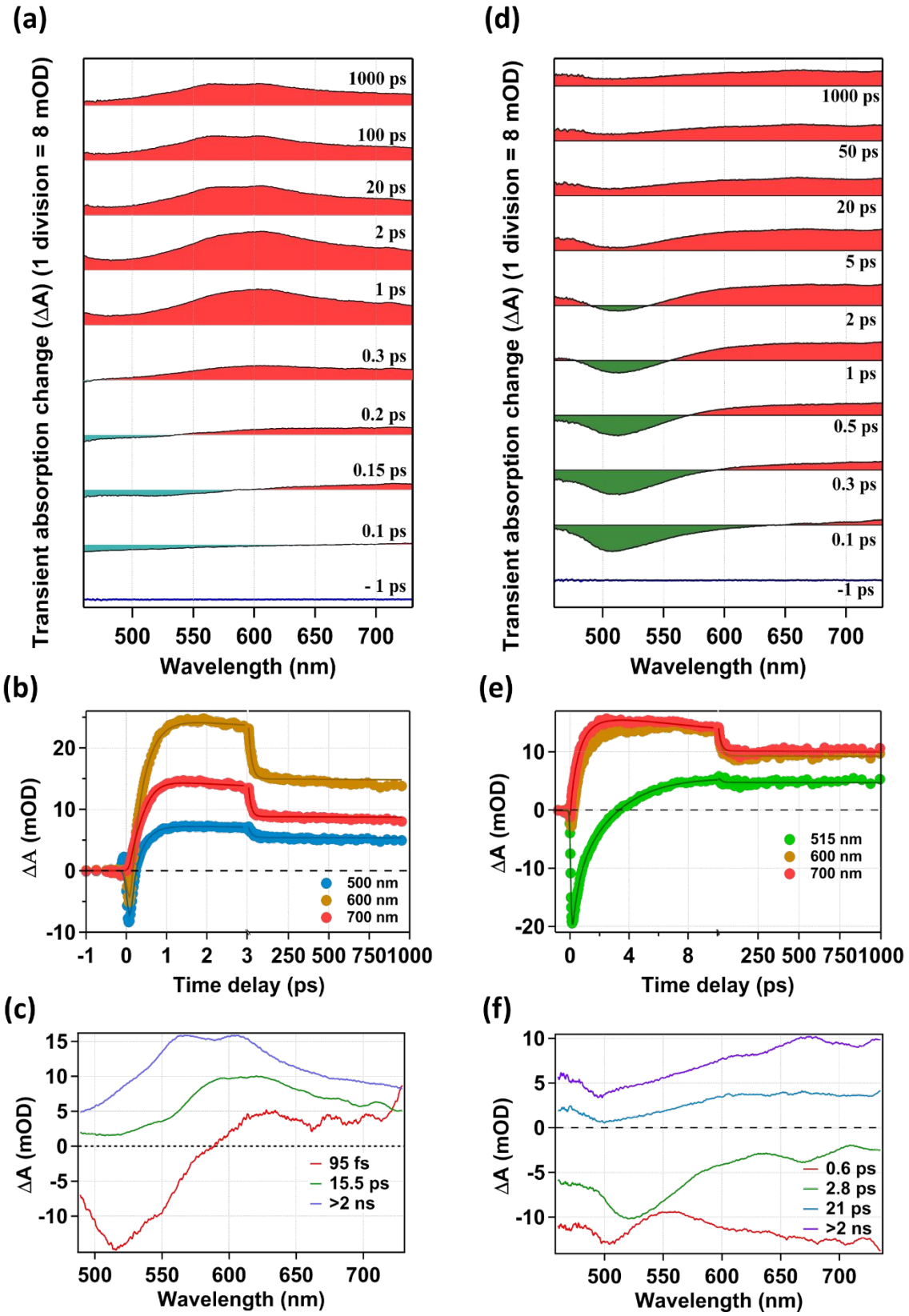


Figure 5. Transient absorption response (pump, 400 nm, probe, 460-730 nm) of TC1 in hexane (left panel) and acetonitrile (right panel). (a, d) TA spectra at some representative delay times for hexane (Hex) and acetonitrile (ACN) respectively. In Hex, the TA spectra consist of extremely feeble SE around 500 nm (cyan) and strong ESA over the whole probe spectral window (red). In ACN, spectra

consist of SE around 520 nm (Green) and ESA above 600 nm (red) . (b, e) Fitted kinetics of TC1 in Hex and ACN solvent at three selective wavelengths of the whole probe window spectra. (c, f) Decay-associated spectra from the global analysis of TA data in Hex and ACN solvent. For TC1 in Hex solvent, three global time constants are 95 fs, 15.5 ps, and > 2 ns, and in ACN solvent, four global time constants are 0.6 ps, 2.8 ps, 21 ps, and > 2 ns. Both the transient measurements were done in aerated condition.

To get a better idea of the involvement of a number of excited states in the photophysical process of TC1, we performed global analysis of TA data to identify the decay-associated spectra (DAS). Figure 5c presents three DAS obtained for TC1 in hexane. The DAS for the 95 fs component has a strong SE feature, while the 15.5 ps and >2 ns components have a prominent ESA features, where the amplitude and sharpness of the former are smaller compared to the latter. On the other hand, we observed four DAS components for TC1 in acetonitrile (see Figure 5f), where the fast components (0.6 ps and 2.8 ps) are of SE type, and the other two components (21 ps and >2 ns) are of ESA type. The 2.8 ps DAS matches well with the steady-state emission spectrum, while the 600 fs DAS probably represents the other short-lived emissive state, we proposed above. The spectral features of the long-lived DAS (21 ps and >2 ns) are broad in nature. The >2 ns DAS has been assigned to the lowest triplet state (T_1) for both in hexane and acetonitrile. The 15.5 ps and 21 ps components of TC1 in hexane and acetonitrile, respectively, are of ESA type. We presume these are the higher triplet states (T_n), which convert to the T_1 state via internal conversion (IC). Similar DAS components (two SE type and two ESA type) has also been obtained for TC1 in dichloromethane (see Figures S8c in SI), and we assign them in the same line as in acetonitrile. It has also been observed that by changing the polarity of the solvents from Hexane to DCM to ACN, the hump position becomes red-shifted, suggesting that the T_1 state has $\pi - \pi^*$ character.

If the proposition of two emissive states having different lifetimes in TC1 is true, one should observe a shift in the fluorescence spectrum as a function of time. At early time, the emission will be observed from both the states, whereas, at the later time, emission will be observed only from the long-lived state. To check the same we re-constructed the time resolved emission spectra (TRES) from the measured fluorescence decays at different wavelengths throughout the emission band (see Figure 6a,b). Consistent with the above expectation, a small change in the spectral maximum was observed. However, as acetonitrile is a polar solvent, it may also solvate the excited state of TC1 leading to a shift in the emission spectrum, that contributes to the observed shift. Nevertheless, the observed dynamics of spectral shift found to be quite slow (10-12 ps) compared to the computed peak frequency shift due to the solvation dynamics in

acetonitrile using the bi-exponential solvation time constants of 0.089 ps (69%) and 0.63 ps (31%)[65] as shown in Figure 6c. In addition, it has also been observed that after photoexcitation the peak frequency marginally shifts until 1 ps (see Figure S9 of the SI), which indicate that the LE state of TC1 achieved through 400 nm excitation is not solvatochromic in nature. Overall, the results authenticate the proposition of the existence of two singlet emissive states in TC1.

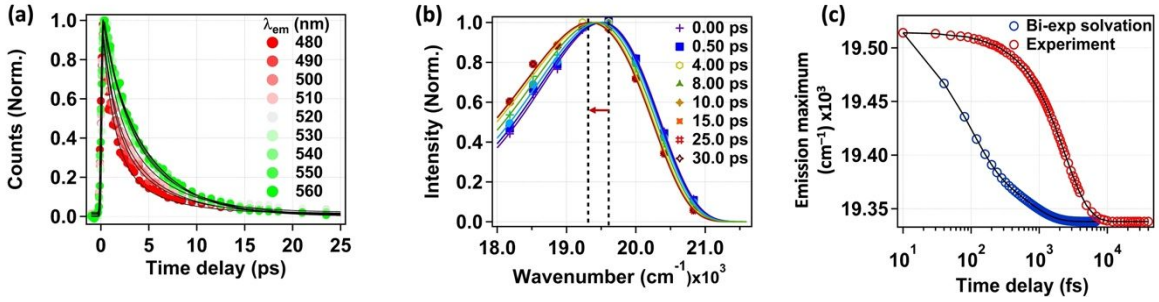


Figure 6. (a) Fluorescence lifetime decay of TC1 in acetonitrile at various emission wavelengths (480-560 nm) in Fluorescence Up-conversion. (λ_{ex}=400 nm) (b) Time-resolved emission spectra (TRES) of TC1 in ACN are constructed from the fitted coefficients of the fluorescence transients (c) Comparison of time-dependent fluorescence peak frequency shift and excited state solvation dynamics related peak frequency shift simulated from the bi-exponential solvation time constants of 0.089 ps (69%) and 0.63 ps (31%)[65]. The TRES shows that the fluorescence peak frequency shift is occurring up to 10-12 ps. All the fluorescence decays were measured in aerated condition.

Steady-state and time-resolved absorption/emission studies within a confined capsule. Octa acid is known to form closed capsular host-guest capsular complexes with varieties of guest molecules.[42-43, 45] The use of OA as host allows us to examine the excited state dynamics of TC1 within a highly confined non-polar OA capsule. Given that excited thioketones are known to be highly reactive in organic solvent media and relax through interaction with C—H bonds of solvents,[12-13, 66-67] a well defined and restricted environment medium is appropriate to gain a better insight into the excited state dynamics of TC1. Recently we established by ^{1}H NMR that OA forms a 2:1 host-guest complex with TC1 in borate buffer solution (pH 7.4).[46] In this study, steady-state absorption and fluorescence measurements were utilized to monitor the binding of TC1 to OA cavity (Figures S10a,b of the SI). A drastic change in the absorption and fluorescence characteristics of TC1 was observed when OA was added to TC1 in water (borate buffer). Consistent with our previous work,[68] the above experiments suggested that the formation of OA–TC1 capsular complex is a two step process (see Figures S10c,d of the SI).

The binding constant for the formation of 1:1 complex (TC1@OA) is estimated to be 2.5×10^5 M^{-1}, whereas, the binding constant of the 1:2 (guest to host; TC1@OA_2)) complex is quite high (3.1×10^{11} M^{-2}). For a solution of 3 μM TC1 and 17 μM OA, the amount of free TC1, 1:1 complex (TC1@OA) and 1:2 complex (TC1@OA_2) are estimated to be <1%, 3% and 96%, respectively.

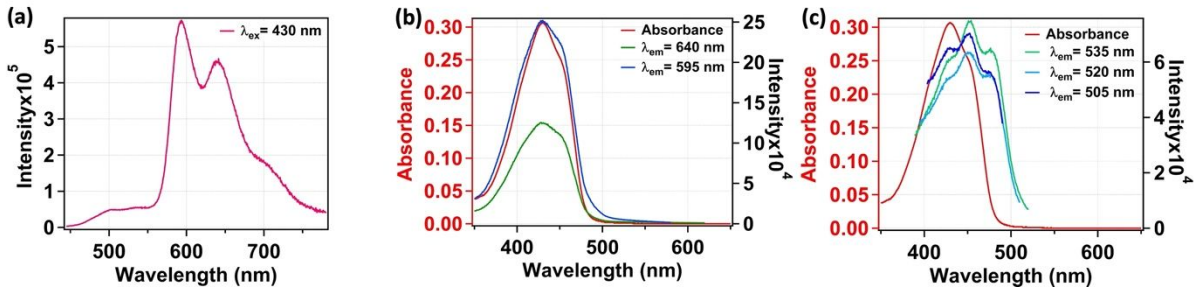


Figure 7. (a) Steady-state emission spectra of TC1 inside the octa acid (OA) cavity in borate buffer solution (excitation wavelength 430 nm) at room temperature; (b) Excitation spectra for the 595 and 640 nm emission bands and comparison with the absorption spectrum; (c) Excitation spectra for three different fluorescence emission regions (505, 520, and 535 nm) and comparison with the absorption spectrum. All the measurements were done in aerated condition.

The steady-state emission spectra of TC1@OA_2 exibits a strong band in 560-750 nm region and a weak band around 490-550 nm (see Figure 7a). The band above 550 nm resembles the phosphorescence measured under nitrogen purged condition in hexane (Figure 2a). Thus, we assigned the low energy band as phosphorescence, and the high energy band as fluorescence. The excitation spectra for both the emission bands are shown in Figures 7b,c. The excitation spectra for the phosphorescence band match very well with the absorption spectrum of TC1. On the other hand, the excitation spectra for the fluorescence band are found to be red-shifted to the absorption spectrum. These results undoubtedly suggest that the fluorescence is mainly originating from a low lying singlet excited state, while the phosphorescence is mainly coupled to the high energy singlet exited state through ISC. This suggests that the internal conversion from upper to lower singlet is slower than ISC. Further, the probability of transition from the ground state to the high energy singlet state is higher compared to the same to the low energy singlet excited state. Thus, the study of TC1 within OA cavity helps us to prove the existence of two closely spaced excited singlet states. The state with high transition probability from the

ground state have the higher energy and is dark. This high energy state is mainly responsible for the generation of triplets, leading to the observation of phosphorescence. The low energy state is somewhat bright state but have very low transition probability from the ground state. This state is mainly responsible for the fluorescence.

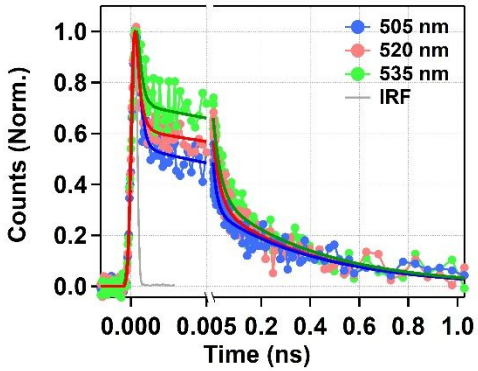


Figure 8. Normalized fluorescence decays of TC1 inside the octa acid (OA) cavity at three emission wavelengths: 505 (blue), 520 (red), and 535 nm (green) (λ_{ex}=400 nm) at 25 °C. All the measurements are done in nitrogen-purged conditions.

The fluorescence lifetime of TC1 in OA cavity monitored at selected wavelengths were fitted into three components (0.3 ps, 30 ps and 420 ps; see Figure 8, fitted parameters are tabulated in Table S5 of the SI). Within the OA cavity, the singlet state lifetime of TC1 is found to be ultrafast, similar to that in hexane. The two fast time components (0.3 ps, 30 ps) were assigned to the two nearly degenerate singlet states. The long component (420 ps) most likely is due to the contribution of phosphorescence.

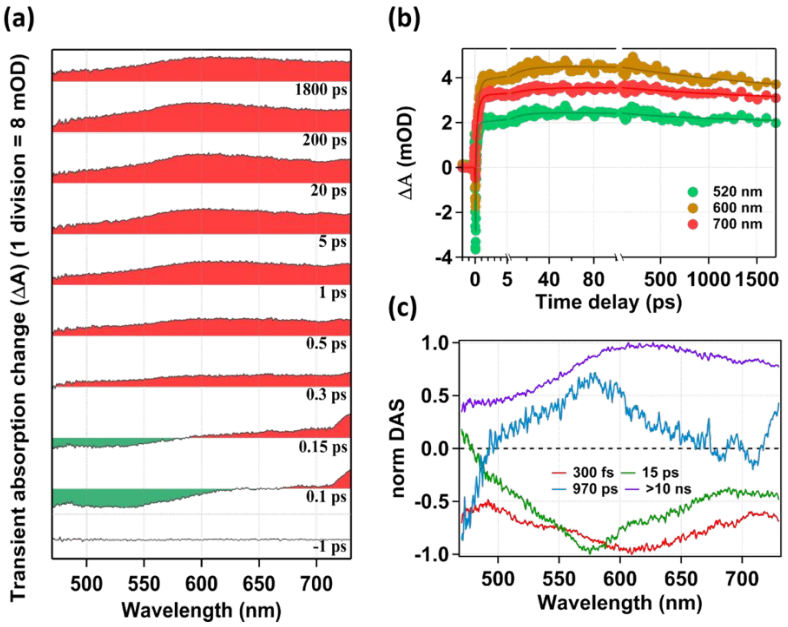


Figure 9. Transient absorption response (pump, 400 nm, probe, 460-730 nm) of TC1 inside the octa acid (OA) cavity. (a) TA spectra at some representative delay times. In the OA cavity, the TA spectra consist of SE around 480-550 nm (Green) and ESA above 600 nm (red). (b) Fitted kinetics of TC1 in OA at three selective wavelengths of the whole probe window spectra. (520, 600, and 700 nm) (c) Decay-associated spectra from the global analysis of TA data in octa acid (OA). For TC1 in OA, four global time constants are 300 fs, 15 ps, 970 ps, and > 10 ns. The transient measurement was performed in N_2-purged condition.

The TA spectra of TC1@OA_2 have a SE band in 480-550 nm region in the early time, which converted to a broad ESA band at later time (see Figure 9a). The transient spectral analysis shows that the SE band is short lived, and the triplet-related ESA arises quickly. To understand the timescale of excited state processes, we performed the kinetic analysis of the transient data in three selective wavelengths i.e. 520, 600, and 700 nm (see Figure 9b). From the fitted parameters of the transient data (See Table S6) we see two rise time components (~0.3 ps and 15 ps) in the triplet state formation, indicating a ultrafast population growth of the triplets. From the global analysis of the TA data we found four DAS components of TC1 in OA capsule (see Figure 9c). The time component of DAS suggests that the first two components (300 fs and 15 ps) are SE type, and the other two components (970 ps and >10 ns) are ESA type. The results show that inside the OA cavity the rate of ISC is extremely fast (~10^{11} s^{-1}), which is probably due to the non-polar environment of the cavity.[69] The results within OA capsule resembles those in hexane. It is known that the capsular interior is non-polar. A comparison

of the results in the three solvents (hexane, acetonitrile and dichloromethane) and within OA cavity suggest that the excited state dynamics of TC1 is highly dependent on the polarity of the solvent. Given that the excited state electronic nature may be subjected to charge transfer from the 7-amino group to the thiocarbonyl side, such a solvent dependence is not unanticipated. To gain a better understanding of the excited state manifold of TC1 and the origin of ultrafast ISC, we performed TDDFT calculations whose results are presented below.

TDDFT calculation. Spectra of of TC1 in acetonitrile computed using TDDFT and the cLR-PCM method, revealed two closely spaced singlet states, S_1 (2.86 eV) and S_2 (2.92 eV), with nπ* and ππ* characters, respectively, at the Franck-Condon (FC) point (see Figure S11 and Tables S7,8 of the SI). The latter state is brighter and also involves intramolecular charge transfer from the amino to the thiolactone end, similar to that reported in substituted coumarins.[70] This is consistent with the larger dipole moment for the excited state inferred in the experiments above. The first two singlet excited states are 0.6 eV apart in the gas phase. However, they are brought closer together in a polar solvent by opposite solvatochromic effects (~0.3 eV) on the two states (also see Table S11). The presence of diethylamino group at the 7-position promotes charge transfer across TC1 upon excitation, subsequently leading to the large solvatochromic effect and the subsequent reduction of the S_1 - S_2 gap. The latter effect is robust to the details of the DFT method applied (see Tables S9 and S10). It is tempting to assign these two states as the two closely spaced singlets responsible for the difference between absorption and excitation spectra of fluorescence. However, given that a similar behaviour is also observed in OA, where the environment is presumably non-polar, it is unclear whether the same two states would continue to be responsible. One possibility is that these two states are also proximal within OA due to interaction of excited charge densities with the OA cage. However, given the expense entailed in computation of TDDF spectra for the OA bound TC1 molecule, we are yet to confirm this possibility.

From the calculations we observed that the triplet state T_2 is only 0.35 eV away from S_2, while the T_3 state is degenerate with S_1 and T_1 is about 0.87 eV below it. The proximity of the T_2 and T_3 states to the first two excited singlet states suggests the possibility of a population transition between the two spin channels. To assess the orbital feasibility of ISC using the El-Sayed rule, frontier molecular orbitals of TC1 in acetonitrile at the FC geometry were computed for different electronic states (see Figure 10). The S_2/T_2 transition is found to be of ππ*→nπ*

character, while, the S_2/T_3 transition have the ππ*→ππ* character. Therefore, the $S_2 \rightarrow T_2$ transition is both energetically and orbitally feasible. Similarly, both S_1/T_3 and S_1/T_1 are characterized by nπ*→ππ*, making them also feasible. The conclusion drawn here parallels the one proposed recently for thionucleobases. In the latter systems also the fast ISC from excited singlet to triplet manifold is attributed to the heavy mixing of nπ* and ππ* triplet states. However, the role of the charge transfer contribution of the diamino group at the 7 position in effecting a fast ISC is not obvious.

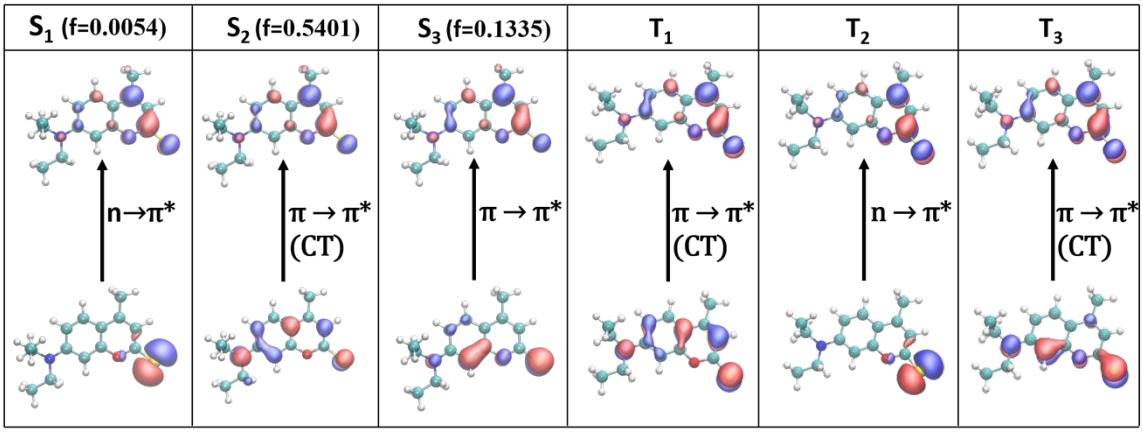
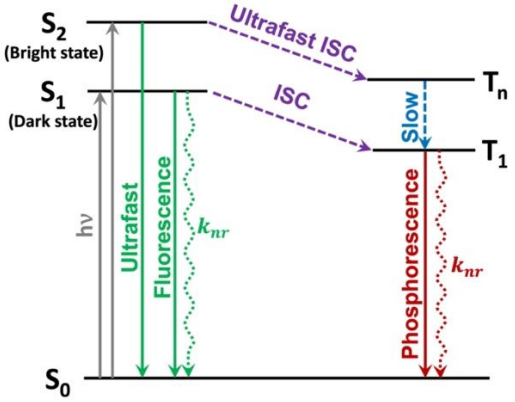


Figure 10. Electronic structure of the S_1,S_2,S_3,T_1,T_2, and T_3 state of TC1 in ACN through TDDFT calculation. A significant change in orbital character in the transition between S_2 to T_2 (ππ* → nπ*) However, there is no change in the orbital character in the transition between S_2 to T_3 (ππ* → ππ*), and S_2 to T_1 (ππ* → ππ*) transition. So, the S_2/T_2 transition follows the El Sayed rule of intersystem crossing (ISC). Similarly, S_1/T_1 transition has orbital character nπ* → ππ* and thus follows El Sayed rule. In the figure, charge transfer transitions are written as CT in short and the values of the oscillator strength of different transitions is written with the symbol f)

The theoretical results presented here are consistent with our experimental observations of fast ISC. Although we have confirmed the existence of fast ISC in TC1 we are unable to unequivocally identify the origin. In general, molecules possessing thiocarbonyl chromophore are reported to have almost unit quantum yield of ISC from excited singlet state. Early studies on thioketones revealed the occurrence of quantitative and fast ISC from both S_2 and S_1.[4, 12-13, 32] In these cases the energy gap between the two states ranges between 35 to 50 kcal/mole. Apart from heavy atom effect due to sulfur, the rapid and quantitative intersystem crossing in alicyclic thioketones from S_2 is suggested to be facilitated by intramolecular C—H vibration.[52]

Thioesters and thiocoumarins possessing O-(C=S) chromophore were also reported to undergo quantitative and rapid ISC from excited singlet state.[40, 47] Unlike in thioketones, in these molcules the gap between S_2 and S_1 is small (5-10 kcal/mole). This makes identification of the electronic nature of the states involved in crossing difficult. In TC the fast and effiecient ISC is attributed to mixing of nπ* and ππ* states and heavy atom effect.[47] One of the most extensively studied thiocarbonyl system is sulfur substituted thio-nucleobases N-(C=S). These molecules also, similar to other thiocarbonyl derivatives, possess ultra short singlet lifetime and quantitative ISC. Because of the close energies of S_2 and S_1, in these molecules also it is not easy to pindown the electronic identity of the S_2, S_1, T_2, and T_1. Because of the closeness, all these states are likely to have both nπ* and ππ* characters. This mixing of states is thought to be the reason for the fast and quantitative ISC in thio-nucleobases.[49-50] Similiarity between thiocoumarins, thioesters and thio-nucleobases is obvious. Clearly replacing the 'O' with 'S' in all these systems, independent of the energy gap between S_2 and S_1, leads to fast and quantitative ISC. In our opinion, there is something more than Kasha's heavy atom effect and El-Sayed's orbital mixing[71] that is responsible for the unusual and interesting excited state properties of thiocarbonyl compounds.



Scheme 2. Schematic representation of possible relaxation pathway of TC1.

Conclusions

The steady-state experiment reveals weak fluorescence quantum yield and room-temperature phosphorescence (RTP) behavior of TC1 in bulk solvents like hexane, acetonitrile and dichloromethane, which are distinctly different compared to the oxygen analogue, C1. This

structural modification also changes the electronic energy levels, and an appearance of two decoupled singlet states with a very short lifetime (sub-ps to ps) has been noticed. Out of these two states, the state with a high absorption coefficient displays low fluorescence characteristics and vice-versa. Fluorescence upconversion measurement in bulk solvent reveals that the photoexcited singlet states of TC1 only sustains up to several picoseconds, indicating extensive population loss in a very short time. Detailed femtosecond transient absorption (TA) study reveals an ultrafast (sub-ps) ISC process is probably the major non-radiative channels operating in the excited singlet state of the molecule. Furthermore, TA analysis reveals that both singlet states play a role in the formation of triplet populations. Higher-order triplets integrate into the lowest triplet state through the IC mechanism in 10s of picoseconds. Inside the isolated octa acid (OA) media, TC1 shows very strong phosphorescence along with a weak fluorescence, which further enunciate our proposition.

The excitation spectral measurement for fluorescence and phosphorescence bands deciphers their different origins on photoexcited singlet states and supports the speculation of decoupled singlet states involved in the ISC process. Fluorescence lifetime measurement inside the OA cavity has revealed a similar bulk solvent-like ultrashort lifetime of the singlet manifolds. TA analysis reveals the ultrafast triplet generation characteristics inside the OA cavity. Theoretical calculations of vertical transition energies in bulk ACN solvent depict the presence of two closely spaced singlets. The low energy gap and the required orbital characteristics of singlet-triplet transition allow us to support the experimental observation of fast ISC behavior. A more detailed theoretical analysis will be reported in a subsequent study.

ASSOCIATED CONTENT

Supporting Information: Synthesis of thiocoumarin-1, theoretical and experimental absorption maxima, emission maxima, and fluorescence quantum yield of TC1 in different solvents, molar extinction coefficient (ε), steady-state emission of TC1 in acetonitrile (ACN) in aerated, nitrogen and oxygen-saturated conditions, steady-state non-gated low temperature (77 K) emission, steady-state excitation spectrum of TC1 in dichloromethane (DCM) and dimethylsulphoxide (DMSO), steady-state absorption, emission, excitation spectra of coumarin 1 in hexane (Hex) and acetonitrile (ACN), excitation wavelength dependent fluorescence quantum yield (ϕ_f) of TC1 in ACN, Decay parameters of TC1, excitation spectra of TC1 in DCM at two different emission wavelengths, steady-state emission spectra of TC1

in ACN at various excitation wavelengths, match of the inverted steady-state emission spectra of TC1 with the time-resolved SE bands from the TA measurement, transient absorption (TA) response of TC1 in dichloromethane (DCM), fitted data of single point kinetic analysis of TC1 in specified solvents at three mentioned wavelengths, time-dependent fluorescence peak frequency shift related to the solvation of the excited TC1 in acetonitrile (ACN), titration of TC1 with octa acid (OA) and binding constant determination, fitted kinetic parameters of the fluorescence decay of TC1 inside the octa acid, fitted data of single point TA kinetic analysis of TC1 inside the octa acid, vertical electronic excitation energies of low-lying electronic states TC1 in acetonitrile (ACN) in (cLR-) PCM method, vertical excitation energies of TC1 to singlet states in gas phase and in acetonitrile, vertical excitation energies of TC1 to triplet states in gas phase and in acetonitrile, comparison of vertical excitation energies of TC1 across various exchange-correlation functionals using (LR-)PCM method.

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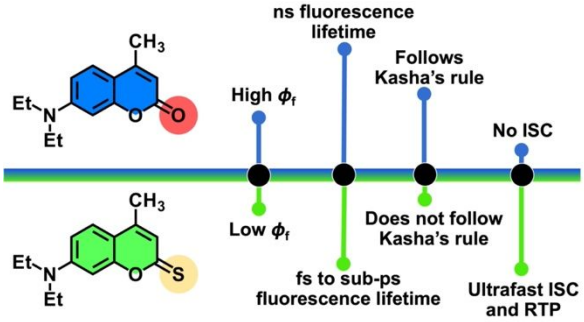
TOC Graphic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