

Comprehensive spectroscopic analysis of energy inversion of the lowest singlet and triplet excited states in the heptazine HzTFEX2

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Comprehensive spectroscopic analysis of energy inversion of the lowest singlet and triplet excited states in the heptazine HzTFEX₂

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Abstract

Detailed photophysical measurements of the non-symmetric heptazine, HzTFEX₂, previously reported as having inverted S₁-T₁ levels, show complex behaviour, highly dependent on environment, concentration and aggregation. Single crystals of HzTFEX₂ show anti-Kasha S₀←S₂ and excimer emission. Solution state absorption shows hypsochromic shifts of the π-π* S₀→S₁, linearly dependent on solvent polarizability. In most environments, emission is dominated by excimer species, only in toluene and frozen 2-MeTHF do monomeric properties dominate. In frozen solutions, aggregation phenomena are solvent dependent. Given such complexity, time-dependent emission spectra are crowded, making it difficult to resolve monomeric phosphorescence. However, by exciting S₀→S₂, we observe a consistent phosphorescence signal at 425 nm, lying 110±20 meV above the S₁ singlet emission. Importantly, exciting S₀→S₁ does not give phosphorescence or delayed emission (DF). We conclude that coupling between S₂ and S₁ is very weak, S₂-T_N intersystem crossing (ISC) is effective, whereas S₁↔T₁ intersystem crossing is highly ineffective because vibronic coupling is negligible at 77 K, fulfilling the conditions required for inverted phosphorescence to be observable. At room temperature, no long-lived DF is observed because vibrational coupling is now strong enough to drive exothermic T₁→S₁ ISC, such that in an OLED high efficiency can be achieved.

Introduction

Since the first theoretical reports of molecular structures that could potentially break Hund's rule¹⁻⁴, hereby the lowest energy singlet state of the molecule lies energetically below the lowest triplet state, i.e. inversion of the singlet and triplet state energy ordering, there has been a flurry of theoretical studies arguing both for⁵⁻¹¹ and against¹² the existence of inversion. Most attention has focused on the heptazine core molecules, with

many theoretical reports outlining molecules with single states lying below the triplet level by between a few 10s of meV to > 250 meV. However, inversion has only been shown using theoretical models based on multi configurational states which include doubly excited excitations, while normal single CI type TD-DFT calculations invariably give non-inverted structures. There has been at least one report that questions the validity of these 2nd order calculations, by going to even higher multi-configurational order calculations, including triplet excited states, showing that inversion is lost in this case. In their paper¹², Dreuw and Hoffmann also point out that, in all the preceding works, calculations were only made in vacuum and did not take any effects of the surrounding medium on the excited state energy levels into consideration. Further, intermolecular interactions have been largely ignored⁵. Experimentally, there are very few reports in the literature giving unambiguous evidence for or against inversion¹³. This is not surprising given the difficulty in synthesizing candidate heptazines which are soluble,^{14,15} and their general spectroscopical inaccessibility¹⁶, due to their deep UV absorption and extremely low oscillator strength of the $S_0 \rightarrow S_1$ transition. Adachi et al.¹⁷ proposes potential inverted energy levels through kinetic modelling of photophysical measurements in solution, performed over limited spectral ranges and temperatures.

Ehrmaier et al.⁵ has stated that, with T_1 below S_1 , intersystem crossing (ISC) will be unlikely because the transition is forbidden. Therefore, spin orbit coupling (SOC) will be very weak and not greatly enhanced by vibronic coupling due to the rigidity of the heptazine core. However, Dinkelbach et al.⁷ has suggested that vibronic coupling is still active to give moderate ISC and potential reverse ISC (rISC) rates, but ISC will be slower since it is an endothermic process under an inverted regime. Experimentally, it is then important to note that exciting directly the $S_0 \rightarrow S_1$ transition in low concentration solutions should lead to very low singlet and triplet excited state populations, remembering that optical excitation only creates singlet states unless SOC is so large that direct $S_0 \rightarrow T_1$ oscillator strength becomes appreciable¹⁸.

As outlined above, the main problem with studying heptazine systems is the fact that they are both difficult to synthesize and, moreover, usually have poor solubility. One of the key points about Aizawa et al.'s. HzTFEX₂ material (Fig 1a), which has attracted the greatest attention¹⁹, is an increased solubility, however still sparingly soluble, achieved through the attachment of asymmetric solubilizing groups. The asymmetric structure also increases the oscillator strength of the $S_0 \rightarrow S_1$ transition, aiding spectroscopic investigation. However, as we shall show, the moderate solubility still causes extreme problems through the strong propensity of the heptazines to aggregate, which is critical in understanding their optical properties.

Here we study the temperature and time-dependent photophysical properties of HzTFEX₂ in multiple environments, including; dilute to concentrated solution, guest-host films, powders and in single crystals. Only by studying this full range of environments and time regimes can we disentangle absorption and emission arising from isolated molecules

compared to those of aggregate states to gain a direct measurement of the optical transitions of the monomolecular lowest singlet and triplet states. The key to rigorously proving inversion is not the simple observation of an emission band higher in energy than the unambiguously determined lowest singlet state, but as well as this, we must also demonstrate that all of the measured photophysics of the molecule support the possibility of a long lived T_1 triplet population, higher in energy than the lowest energy S_1 singlet state, such that (phosphorescence) emission from this triplet population could be possible. Without this, any result remains ambiguous.

Results

1. Solution state measurements

We first show basic solution-state measurements for HzTFEX₂ to give a baseline for spectral identification. The synthesis and purification of HzTFEX₂ is given in the previous report of Aizawa et al¹⁹.

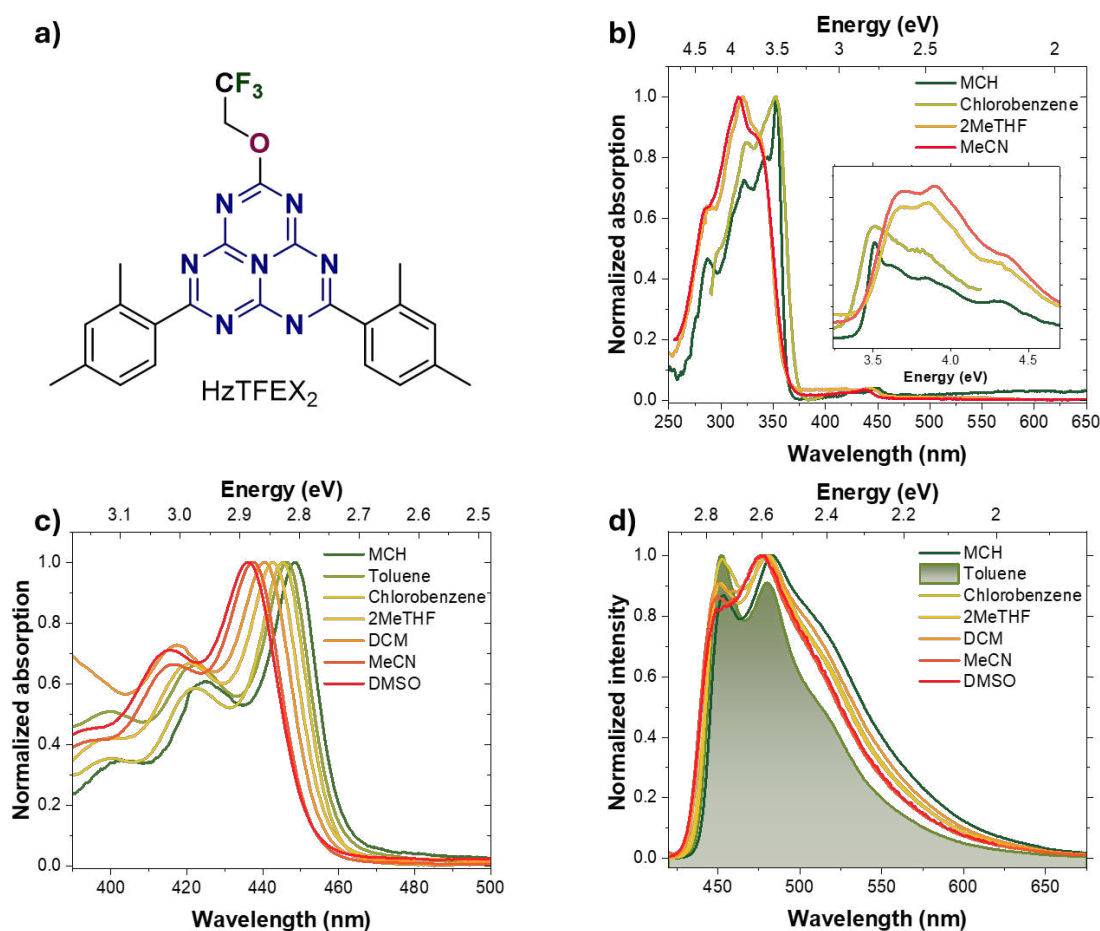


Fig 1. Preliminary photophysical characterization in solution. (a) Molecular structure of HzTFEX₂. Normalized absorption of HzTFEX₂ depicting (b) high energy bands (0.2 μ M) and (c) low energy bands (20 μ M) in a range of solvents. Insert shows UV absorption in energy units (using a Jacobian transform²⁰). (d) Steady-state emission of HzTFEX₂ (20 μ M) in a range of solvents, showing no solvent shift in emission over a wide range of polarities. $\lambda_{\text{ex}} = 355$ nm.

Absorption features are observed in two spectral regions. Below 370 nm we observe high oscillator strength bands which are solvent dependent (Fig 1b). A 360 nm peak is observed in low polarity solvents, but not in high polarity solvents, where a strong 340 nm band is observed. There is a clear difference in the absorption of these high lying states as a function of solvent environment. We believe that the sharp red edge feature indicates potential dimer content in low polarity solvents. Above 400 nm, a far weaker band (Fig 1c) with a well resolved vibronic progression, peak extinction coefficient $2,130 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$ (Fig S1), e.g. 446 nm (2.78 eV) in 20 μM toluene solution measured in a 5 cm pathlength cell. Clearly this is not a small oscillator strength transition, concomitant with a weak π - π^* transition. It also shows significant solvent dependent hypsochromic energy shift. This is the lowest energy absorption band we are able to observe and so is ascribed to the $S_0 \rightarrow S_1$ transition of HzTFEX₂. The singlet character is confirmed by the addition of a 10:1 excess of triplet scavenger, cyclooctatetrene (COT), where such concentration lead to the complete quenching of benzophenone phosphorescence, and saturated oxygenated solution. Both approaches show no quenching of the HzTFEX₂ emission; see SI section 1.1. This assignment then indicates that the 340 nm (peak) absorption must be from the π - π^* $S_0 \rightarrow S_2$ transition, in excellent agreement with the theoretical calculations of Dinkelbach et al.⁷, for a substituted heptazine molecule.

Theory also indicates that the $S_0 \rightarrow S_1$ transition of HzTFEX₂ and other heptazines have π - π^* character, whereas a 75 meV hypsochromic solvent shift at room temperature (RT) was observed here, suggesting n - π^* character, as proposed by Li et al²¹. A smaller 37 meV hypsochromic shift is observed for the emission bands (Fig 1d), saturating at low polarity (Fig S2). The Stokes shift between the lowest absorption band and emission band is very small (36 meV in toluene) (Fig S3), as would be expected for a rigid heptazine core molecule and indicates no obvious charge transfer character to the $S_0 \rightarrow S_1$ transition. However, there are previous reported cases where a π - π^* $S_0 \rightarrow S_1$ transition shows a solvent-dependent hypsochromic shift, particularly for molecules containing sp^2 hybridized nitrogen atoms within a conjugated structure.²² Here, the ground state is strongly localized due to the participation of the localized nitrogen lone pair electrons in the π orbitals, but the excited state is a delocalized π^* state, with the transition of a nitrogen lone pair electron into the π^* orbital being the most likely excitation, thereby not changing the dipole moment of the molecule but increasing its polarizability. A solvent-dependent hypsochromic shift in absorption in this case does not result from solvent polarity, but the polarizability of the solvent molecules. With non-polar solvents; methylcyclohexane (MCH), toluene and dichloromethane (DCM), which have the highest polarizability, we observe a near saturated red shift of the absorption band, but a linear increase of the band energy with decreasing solvent polarizability. The emission band does not change shape and the full band simply shifts in energy. A rather important observation for a proposed inverted molecule.

In emission, we observe a well-structured band having small Stokes shift, with a characteristic peak at 450 nm, which we ascribe to the 0-0 band of the $S_0 \leftarrow S_1$ transition. The first vibrational overtone being at 475 nm. We observe solvent and concentration dependent changes to the intensity ratios of these first two modes (Fig S4). This we ascribed to the effect of underlying dimer/aggregate-like emission, which broadens and red shifts the monomer 0-1 emission band, and is an important signature of aggregation in solutions. Toluene consistently shows the most intense 0-0 emission feature and has the smallest aggregate contribution (effectively zero below 20 μM concentrations, Fig S4a) whereas in 2-MeTHF we observe increased aggregate contribution at lower concentrations, above 1 μM (Fig S4b). Aggregation mostly increases at 80 K, in frozen solvent (Fig S5). This will be elucidated as we proceed through the paper. Self-absorption is not a problem in these spectra, since no red shift of the highest energy emission band up to 20 μM is observed, unsurprising giving the low extinction of the $S_0 \rightarrow S_1$ transition.

From the toluene spectra we calculate a vibronic spacing of 1340 cm^{-1} , a softer N-C stretching coupling mode than calculated by Dinkelbach et al⁷. As a guide to the general emission efficiency, we measured a 2 μM 2-MeTHF solution of HzTFEX₂ at room temperature, both aerated and degassed (bubbling with argon (Ar) for 20 mins). Photoluminescence quantum yield (PLQY) is excitation dependent, ranging from 0.33 ± 0.05 to 0.42 ± 0.05 in air saturated solution, with an enhancement of $\approx 20\%$ when O₂ is removed. At 80 K, PLQY increases to near unity. Further details are given in SI section 1.2. Given the long lifetime of prompt emission from HzTFEX₂, (described later in the paper) the small difference between aerated and degassed PLQY can be accounted for by oxygen singlet quenching as well as some possible delayed fluorescence (DF) contribution quenching²³. These are high values of PLQY and show how the asymmetric substitution of the heptazine core in HzTFEX₂ lifts the forbidden nature of the $S_0 \leftarrow S_1$ decay. It also shows that at low temperature, all vibrationally coupled processes are effectively quenched for the S_1 state, i.e. internal conversion and intersystem crossing.

2. HzTFEX₂ Crystal state.

High-quality single crystals of HzTFEX₂ were grown by slow evaporation of saturated 2Me-THF solution (see SI section 2). The triclinic crystals of P1 space group have no co-facial overlap of the heptazine cores in any direction, but there is overlap between adjacent cores and periphery phenyl rings with minimum spacing of $3.35\text{ \AA}$, bearing a pseudo head-to-tail configuration because of the fluorine containing peripheral substituents. This arrangement can yield molecular pairs having J-like exciton coupling²⁴ that are emissive (Fig 2a). Globally, the molecules organize in layered sheets spaced by roughly $12\text{ \AA}$ (Fig S9), demonstrating how the fluorine-containing peripheral groups hinder the tail-to-tail intermolecular interactions.

Spectroscopically, we observe two emission bands from the crystals (Fig 2b and S10), one to lower energy, peak 485 nm, with a weak vibronic structure, and a small blue

shoulder at 450-460 nm. These features are similar to those observed in solution and we again ascribe the 450-460 nm shoulder to the $S_0 \leftarrow S_1$ transition, and the strong 485 nm band to dimer like emission. However, surprisingly, we also find a second high energy emission band, peak 380 nm, with vibronic structure very similar to the $S_0 \leftarrow S_1$ transition, whose intensity strongly depends on excitation wavelength, being only weakly observed above 350 nm excitation. This band we ascribe to an anti-Kasha $S_0 \leftarrow S_2$ radiative transition²⁵, following the energetic state ordering of Dinkelbach et al⁷. Both bands have different polarization directions of the emission transition dipole moment and so we ascribe them to emanate from different excited state species, which also allows us to observe the UV emission in the crystal phase, as self-absorption is avoided in certain directions. Time-resolved emission spectra were measured at different temperatures (300, 80 and 20 K) using 355 nm excitation as shown in Fig 2d-f, depicting a rapid decay of the $S_0 \leftarrow S_2$ emission band, $\tau_{S_2} < 2$ ns. The $S_0 \leftarrow S_1$ blue shoulder, 450-460 nm, decays at a comparably rate as the $S_0 \leftarrow S_2$ emission close to our time resolution and is ascribed to rapid quenching of excited monomers; note that we have to use a 360 nm laser rejection filter for time-resolved measurements, which partially cuts off $S_0 \leftarrow S_2$ emission. At 20 K (Fig 2f), the $S_0 \leftarrow S_2$ is seen to be more intense but it decays at the same rate as at 300 K. This fast-decaying $S_0 \leftarrow S_2$ band has a small Stokes shift compared to the onset of strong UV absorption seen in solution (Fig. S11). At RT, we further see the emergence of another weak emission band at 520 nm as the intensity of the 485 nm band decays, after ca. 50 ns. This potentially is emission from another dimer species in the crystal. Excitation spectra are also given (Fig 2c). The 485 nm species has a lifetime greater than 100 ns, consistent with emission from a weakly interacting intermolecular head-to-tail state in the crystal.

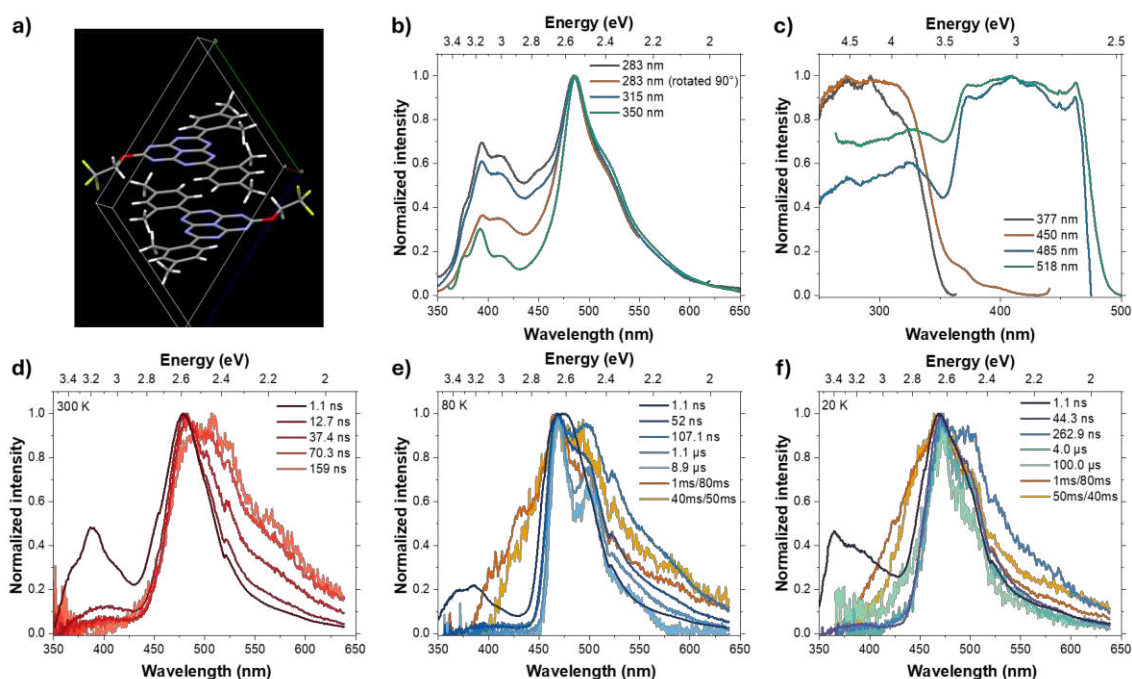


Fig 2. Single crystal characterization. (a) Crystal structure of HzTFEX₂ depicting the packing motif. CIF file has been deposited with the Cambridge Structural Database, CCDC 2551605. (b) PL of a single crystal of HzTFEX₂ monitored at RT. Excitation wavelengths are indicated. (c) Excitation profile of a single crystal of HzTFEX₂ monitored at RT. Monitored wavelengths are indicated. TRPL curves of a single crystal of HzTFEX₂ measured at (d) 300 K, (e) 80 K and (f) 20 K. $\lambda_{\text{ex}} = 355$ nm.

At 80 K (Fig 2e), is initially dominated by the 460 nm monomer with a small 485 nm contribution growing in over the first 50 ns. From this we can see that the 485 nm emitting species is thermally activated and so we ascribe it to an excimer, not dimer. At 20 K (Fig 2f), we see a weak, long-lived remnant of this excimer emission confirming the activated formation mechanism. From around 1 μ s to 50 μ s, after all the initial states have decayed, we observe only the vibronically structure 460 nm band (Fig S12). This lives into the millisecond, but it is very weak at these long times, even at 20 K. This long-lived, highly-structured emission is assumed to be delayed monomer emission arising from triplet-triplet annihilation (TTA). Given that this emission does not noticeably decrease in intensity at 20 K compared to 80 K points to TTA being the source of this emission, not a thermally activated process, however the intensities are far too weak to be able to make a fluence dependence²⁶. At millisecond times, low intensity, broad, gaussian-shaped emission is observed at 80 K and 20 K (Fig 2e and f), having the blue edge at higher energy than monomer emission. It is unrealistic to ascribe this emission to any definite species as it is so weak.

From these measurements it is noticeable that the lowest energy monomer and excimer states strongly overlap leading to a spectrally congested composite emission band which is difficult to deconvolute. In powder samples, we further observe contributions from these excited states, including a prominent long-lived band at 520 nm, see SI section 3.

This species is ascribed to close contact dimers formed in the amorphous regions of the powder samples.

Dilute guest-host films

We next turn to HzTFEX₂ dispersed in an inert host polymer matrix, either polystyrene or zeonex. Very low concentrations of HzTFEX₂ were used to minimize dimer contributions.

Zeonex

Drop-casted films of HzTFEX₂ in the range 0.001% to 1% wt/wt in zeonex were investigated. Excitation and emission spectra of these guest-host films are given in Extended Data Fig 1 and S23-24. In the most dilute cases, emission has well defined vibronic structure with a first vibronic at 455 nm and a second vibronic component at 475 nm, a comparison to dilute toluene solution is given. As the concentration of HzTFEX₂ is increased, we see the diminution of the 455 nm peak and an increase in intensity of a 480 nm band, as observed in the crystal and powder samples, indicating an increasing contribution of excimer content, even at relatively low HzTFEX₂ concentrations. At 0.001% HzTFEX₂ loading, weak S₀←S₂ emission was observed below 410 nm (Fig S24).

Emission and excitation profiles of 0.1% HzTFEX₂ zeonex films, measured as a function of temperature, are shown in Extended Data Fig 1b and S26. The excitation spectra only changes in relative intensity, mirroring changes in emission intensity, with minor shifts at the band edges. The temperature-dependent emission spectra show very similar trends, independent of excitation wavelength. We observe a decrease in monomer S₀←S₁ emission as temperature reduces and a small monotonic blue shift to 450 nm at 80K, which, again, is most probably due to increased underlying excimer emission. The intensity of excimer emission decreases, but less so relative to monomer emission, which could suggest a monomer-excimer equilibrium shifting towards longer-lived excimer species giving rise to more excimer emission and less excimer decaying back to excited monomer states at lower temperature. We note that zeonex acts as a viscous fluid, therefore small movements of guest molecules can occur in the amorphous zeonex matrix.

Time-resolved emission from 0.001% HzTFEX₂ in zeonex films at RT (Extended Data Fig 1c-d) shows a fast-decaying S₀←S₂ emission and the characteristic mixed, long-lived monomer and excimer emission at room temperature, decaying within a few microseconds. At 80 K, we see that the 480 nm excimer band decays more slowly than the 450 nm monomer emission, which lives > 1 μs. Signal rapidly becomes too weak to measure at such concentration. Thus, we increased to 0.1% and 1% HzTFEX₂, noting that this would increase intermolecular state contributions (Extended Data Fig 1e-h). Over the first few microseconds, we observe very similar photophysics as in the 0.001% films, except for reduction of the S₀←S₂ emission, presumable through increased self-absorption at the higher concentration of HzTFEX₂. Fluorescence decay is observed for

increasingly longer delay times as doping content increases (2 μ s and 10 μ s for 0.1% and 1% at 80 K, respectively) (Fig S27-30). We associate this with emission from dimer/aggregate states and, therefore, assume that TTA is active in aggregated sites of the HzTFEX₂ films. Measuring the 0.1% film at 80 K after a delay time (DT) and integration time (IT) of 1 ms and 80 ms, respectively, we observe a new feature on the blue edge of unresolved emission, at ca. 420 nm (Extended Data Fig 1f). Comparable emission is observed from 0.01% film at 20 K (Fig S31). However, spectra captured using the same settings for 1% film gives just a broad signal with 480 nm peak (Extended Data Fig 1h). This indicates that long-lived emission in 0.1% and 0.01% sample is more associated with the monomer species, whereas the 1% originates from aggregates.

Looking more closely at the millisecond behaviour, a new feature at ca. 420 nm is observed in the 0.01% films in the spectra collected with DT = 1 ms and IT = 80 ms. However, the feature becomes weaker when DT = 40 ms. We consider this 420 nm blue edge species to be a candidate monomer phosphorescence, but in these films every spectral signature seems to live longer than a millisecond, so we do not jump to this conclusion. At 20 K, time-resolved spectra (Fig S31), show less structured monomer and dimer emission bands living to ca. 1.25 μ s. Prompt S₀←S₂ emission is also observed at DT = 2 ns. Very long-lived excimer emission > 1 μ s is suppressed, in line with activated formation. With DT and IT of 1 ms and 40 ms, respectively, we see a stronger 420 nm band along with delayed 450 nm monomeric S₀←S₁ emission. As phosphorescence and delayed S₀←S₁ emission occur simultaneously in the millisecond time regime, we assume that this indicates quenching of triplet migration, therefore only a small TTA contribution can be observed in dilute films. However, as we excite via the S₀→S₂ transition, upper triplet states can form via S₂ → T_N, creating a T₁ triplet state population through internal conversion (IC). So, if we have singlet triplet (S₁-T₁) inversion, T₁→S₁ (and S₁→ T₁) ISC must be extremely slow to allow the observation of such long lived triplet emission, indicating a forbidden ISC process that requires activation by vibrational coupling. Dinkelbach et al.⁷ and Ehrmaier et al.⁵ have proposed that T₁→S₁ ISC must be a vibrationally activated mechanism. This is why we observe such an extremely slow process at 20 K. Similar observations were also found using polystyrene as host matrix; see SI section 4.1.

Temperature-dependent solution measurements

Now that we have highlighted the dominant role of excimer and dimer emission in HzTFEX₂, we return to solution-state measurements armed with this important knowledge. In all cases, solutions are degassed by Ar bubbling to minimize dimer formation. As we have seen, toluene seems to be the best solvent for HzTFEX₂, but does not form a glass when, leading to emission scattering. Instead, we first studied 2-MeTHF, a moderately good solvent for HzTFEX₂, which does form excellent low-temperature glasses. HzTFEX₂ was also studied in acetonitrile and methylcyclohexane to encompass a wide range of solvent polarizabilities. Behaviour in MCH is found in SI section 5.3. We

made measurements starting from room temperature going down to 80K in an effort to minimize the effects of dimer formation.

2-MeTHF solution

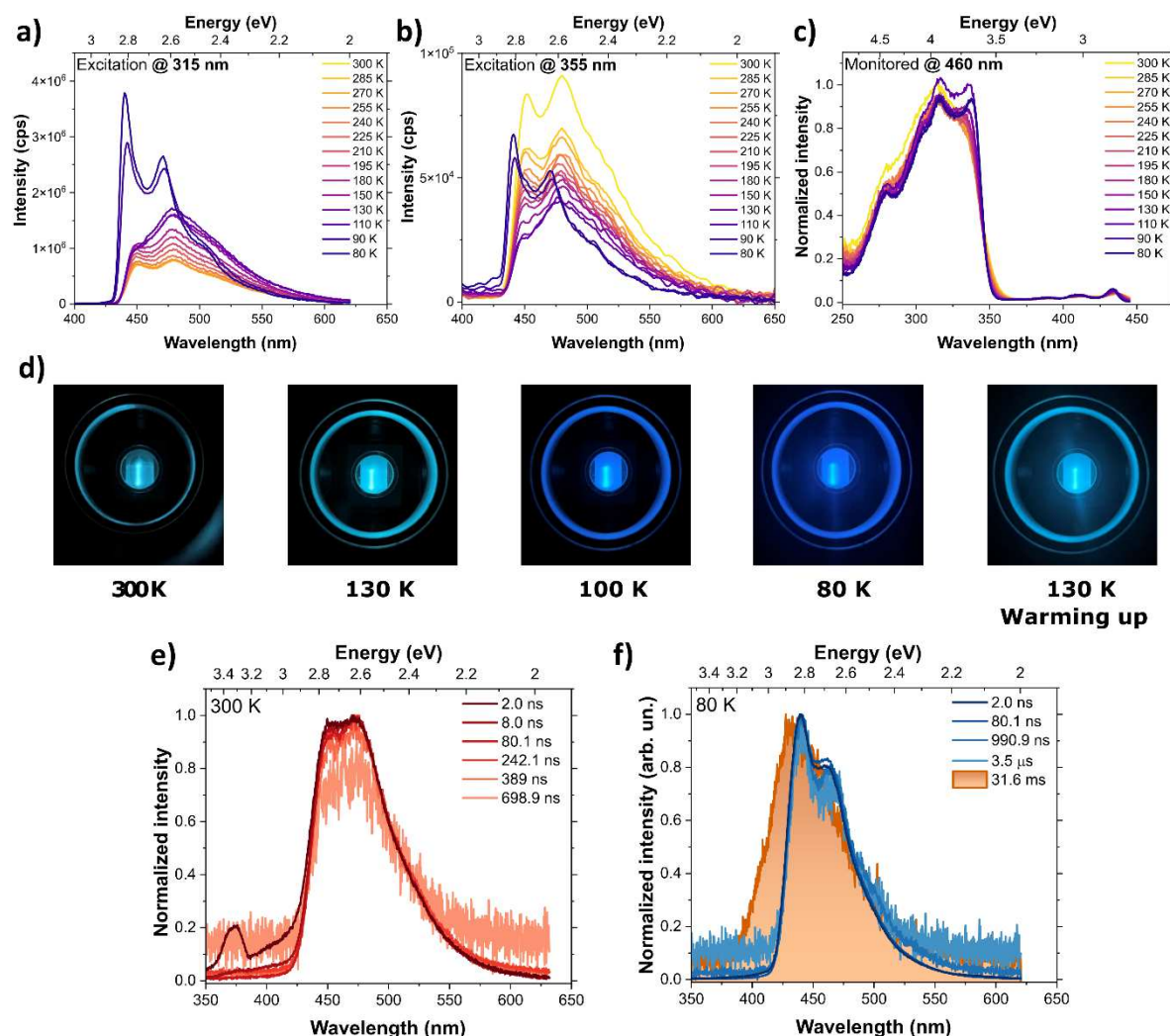


Fig 3. Temperature dependency of photoluminescence in 2-MeTHF solution. PL of H₂TfEX₂ in 2-MeTHF 2 μM air saturated solution monitored in a range of temperatures. **(a)** $\lambda_{\text{ex}} = 315$ nm. **(b)** $\lambda_{\text{ex}} = 355$ nm. **(c)** Excitation profile monitoring emission at 460 nm in a range of temperatures. Signal was corrected by PL intensity. Inset shows zoomed signal between 350 nm to 450 nm. **(d)** Luminescence of the 2-MeTHF solution captured in a range of temperatures. $\lambda_{\text{ex}} = 315$ nm. The temperatures given are those measured above the sample space and the correction applied to reflect the solution temperature inside the quartz cuvette inside the cryostat is described in SI section 5.1. TRPL of H₂TfEX₂ in 2-MeTHF 2 μM air saturated solution monitored at **(e)** room temperature and **(f)** 80 K. $\lambda_{\text{ex}} = 337$ nm.

Exciting the $S_0 \rightarrow S_2$ transition at 315 nm we observe the normal combination of monomer emission (450 nm) and excimer contribution (480 nm), even at 2 μM (Fig 3a). As the solution cools, excimer intensity increases strongly and emission from the dimer species at 520 nm emerges as well. We see no shift in the emission band position as temperature decreases, even though the polarity/polarizability of 2-MeTHF changes as a function of

temperature²⁷, showing that these solvent charges have no effect on the excited state properties of the HzTFEX₂, confirming no excited-state charge-transfer character.

We observe an increasing absorption ‘spike’ on the red edge of the S₀→S₂ transition in the excitation spectra (Fig 3c and S33), which correlates with increasing dimer emission. When 2-MeTHF freezes, (ca. 100 K measured in the cryostat, explained in SI section 5.1) we observe a near phase-transition, abrupt change in emission spectra, now dominated by a highly vibronically-structured monomer emission, blue shifted to 435 nm (peak). The shift is also clearly observed from the luminescence of the solution (Fig 3d). This blue shift occurs abruptly upon freezing. Concurrently, there is a major, but not complete, loss of excimer emission, which indicates that its formation has been frozen out. However, excimer emission is reinstated when the solution is warmed up to 130 K²⁸. This similar change in band shape is also observed in the crystal emission comparing room temperature to 80 K spectra, Fig 2. Exciting at 355 nm (Fig 3b), at the equi-absorption point for S₀→S₁ and S₀→S₂ transitions, we observe strong monomer, excimer and dimer emission. Upon cooling, we see a general decrease in emission intensity because the strong S₀→S₂ absorption band edge blue shifts, reducing absorption at 355 nm (Fig 3c). Again, the spectrum collapses to a blue-shifted, near pure monomer emission upon freezing, with an underlying dimer red tail. We find a vibronic mode spacing energy of 1460 cm⁻¹, which is harder than the mode observed in the liquid state (1340 cm⁻¹), indicating an increased rigidity of the HzTFEX₂.

Lifetime measurements exhibit a biexponential prompt fluorescence decay at RT (Fig S34). 405 nm excitation (S₀→S₁) yields τ_1 = 20.2 ns (35%) and τ_2 = 80.57 ns (65%), which are altered to τ_1 = 13.47 ns (43%) and τ_2 = 92.39 ns (57%) when solution is degassed. Therefore, lifetimes don’t point to an emission mechanism involving triplet states. Similar bimolecular decay is observed for 320 nm excitation (S₀→S₂). The higher energy component of prompt emission decays at a faster rate, therefore, we extrapolate that the shorter-lived decay component is associated with the quenched monomeric species (through exciplex formation). However, the spectral differences are minimal overtime and inconsistent with the discrepancy in lifetime, which indicates an equilibrium between monomeric and excimer species, where monomer concentration is maintained due to the dissociation of excimer species in fluid solution^{29,30}. This mechanism, on top of the presence of emissive dimers, leads to a complex decay profile. At 80 K (405 nm excitation, S₀→S₁, Fig S34c), a single decay component of 102.6 ns was observed, when predominantly monomer species exist, attributed to monomer S₁→S₀ decay and we regard it as a more accurate representation of radiative emission lifetime, since dynamic quenching mechanisms involving the non-monomeric species are quenched at low temperature³¹. At longer times (330 nm excitation, S₀→S₂, Figure S34d), a decay with τ_{average} = 2.2 μ s is found, corresponding to the delayed emission observed from the time-resolved photoluminescence.

Time-resolved spectra were measured exciting at 337 nm using a 350 nm laser rejection filter. At RT, for 2 μ M solution (Fig S3e), we see a combined decay of the monomer and excimer bands within 1 μ s, having linear power fluence (Fig S35), indicating purely monomolecular decay. Note, our gated delayed emission measurement technique enables us to observe fluorescence decays beyond ten lifetimes³². The monomer band decays at a faster rate relative to the excimer. The same decay profile was observed for direct $S_0 \rightarrow S_1$ excitation at 437 nm (Fig S36). At 80 K (Fig 3f), we observe the vibronically structured blue-shifted monomer prompt emission at 435 nm, with much less excimer emission. This clearly shows that the 435 nm band is still monomer $S_0 \leftarrow S_1$ singlet decay, not fast phosphorescence. We observe that the excimer emission emerges from the 435 nm band as a 480 nm shoulder over several hundred nanoseconds as the monomer emission decays, causing a red shift of the 470 nm $S_0 \leftarrow S_1$ second vibronic. For a DT > 850 ns, excimer contribution decreases, revealing a well-resolved vibronic spectrum that greatly resemble the pure monomer, attributed to monomer delayed fluorescence. At 0.2 μ M concentration (Fig S37), we observe a tail of the $S_0 \leftarrow S_2$ emission (cut in the UV by the laser rejection filter), giving a good estimate of its lifetime at <10ns. At delay times above 10 ms, we do not detect excimer emission with 337 nm excitation, whereas a small contribution is present at 355 nm excitation (Fig S38), consistent with all our measurements at these two excitation wavelengths. However, a monomer like band blue shifted to 425 nm is now observed, consistent with monomer phosphorescence observed in zeonex.

We see that the emission intensity in the 80 K glass increases by a factor of around 2.5 compared to RT, so using the measured degassed RT PLQY of 0.42 ± 0.05 , this yields a PLQY at 80 K of near unity, which we believe shows that suppressing excimer formation greatly increases quantum yield. See section 1.2 in the SI.

Toluene

Toluene is the ‘best’ solvent for HzTFEX₂, by which we mean that it gives the least excimer/dimer formation, even at relative high concentrations. Only above 20 μ M do we see appreciable intermolecular interaction (Fig S43a). Excitation profiles show the overlap between the monomer and dimer absorption bands (Fig 4c and S43b). We observe a well-structured emission of monomer plus a small excimer contribution for a 2 μ M solution when exciting into the $S_0 \rightarrow S_2$ transition (315 nm excitation, Fig 4 and S44). As the temperature decreases, the monomer contribution increases in intensity, whereas the excimer emission decreases, concluded from the $S_0 \leftarrow S_1$ 0-1 vibronic at 475 nm emerging from under the 480 nm dimer band. We also observe a blue shift of the $S_0 \leftarrow S_1$ 0-0 from 455 nm to 445 nm (Figure S45). On freezing, (145 K in the cryostat) intensity drops, potentially due to crazing of the solid solution, but the ratio of 0-0 to 0-1 vibronic bands decreases pointing to increased excimer/dimer contribution. This is clearer when exciting at 355 nm (Fig 4b), where, on freezing, a large increase in 480 nm excimer emission occurs. We also note that the monomer peak shows a 445 nm and 455 nm

contribution. Looking at changes in the excitation spectra (inset Fig 4c), we see that absorption around 440 nm first blue shifts as temperature drops, showing loss of dimer, and becomes broader and red shifted, with increased spectral weight on the red edge, when the solution freezes, indicating higher dimer content. This is also reflected in the $S_0 \rightarrow S_2$ absorption band, where a far clearer growth on the red edge is observed on freezing, indicating the presence of the 520 nm dimer. This is different behaviour to what we saw in 2-MeTHF, but it fits with excimer/dimer quenching of excited monomer states. Förster energy transfer between monomer and dimer species in frozen solution could be responsible for this.

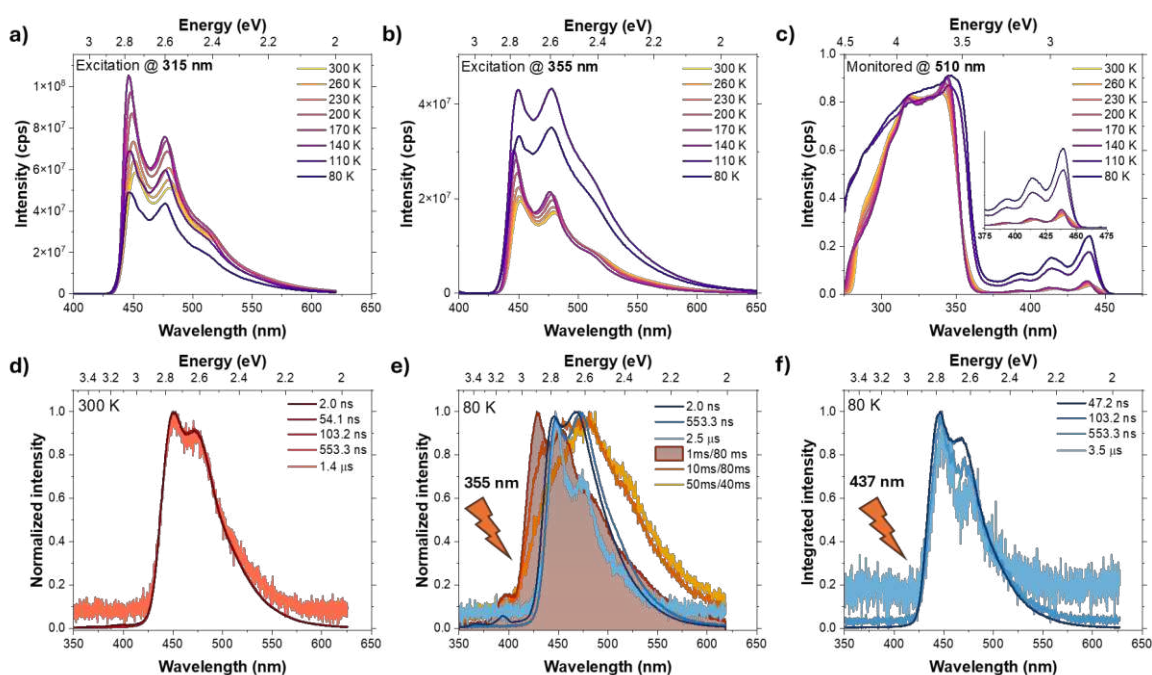


Fig 4. Temperature dependency of photoluminescence in toluene solution. PL of HzTFEX₂ in toluene 2 μM air saturated solution monitored in a range of temperatures. **(a)** $\lambda_{\text{ex}} = 315$ nm. **(b)** $\lambda_{\text{ex}} = 355$ nm. **(c)** Excitation profile monitoring emission at 510 nm in a range of temperatures. Signal was corrected by PL intensity. Inset shows zoomed signal between 375 nm to 475 nm. TRPL of HzTFEX₂ in toluene 2 μM air saturated solution monitored at **(d)** room temperature and **(e,f)** 80 K. **(d,e)** $\lambda_{\text{ex}} = 355$ nm. **(f)** $\lambda_{\text{ex}} = 437$ nm.

Turning to the time-resolved emission at 2 μM concentration, measurement at room temperature (Fig 4d) reveals the usual combined decay of the monomer and excimer emission lasting well into the μs region. This same behaviour is seen with excitation at 337 nm, 355 nm and 437 nm (Fig S46 and 47). The power fluence dependence of the delayed emission is bimolecular at room temperature (Fig S48), showing the classic quadratic turning over to linear, signifying TTA, which is ascribed to a collisional process in fluid solution. On freezing, however, this changes to a pure linear behaviour (Fig S49), signifying the suppression of collisional mechanisms, leaving a monomolecular process generating delayed emission, bearing half the intensity measured from TTA. Exciting at 435 nm, purely into the $S_0 \rightarrow S_1$ transition (Fig 4f and S47), we see faster decay relative to the higher energy excitation. There is little difference in the decay between room temperature and 80 K, but no long-lived delayed emission is seen. This is a very important

observation: we observe far less triplet contribution to the decays when exciting the $S_0 \rightarrow S_1$ transition.

Delayed emission from the monomer is observed after all excimer/dimer have decayed (Fig 4e, DT = 2.5 μ s) when a frozen solution is excited via $S_0 \rightarrow S_2$ (355 nm). The power fluence indicates a monomolecular emission process causing the delayed monomer emission. This again suggests that a large triplet population, initially formed by ISC from S_2 , slowly internally converts down to T_1 and ISC to S_1 very slowly, yielding delayed monomer emission. At the highest excitation powers used (75 μ J) and with a DT = 10 μ s, at RT), we observe a very weak UV emission at 400 nm, (337 nm excitation, Fig S49), which matches the $S_0 \leftarrow S_2$ emission, indicating that some TTA can occur in frozen solutions, presumably in neighbouring dimer or larger aggregate sites. A major change occurs in the millisecond time regime. Measuring with DT = 10 ms and IT = 80 ms (Fig 4e), we observe a highly-structured emission band, a very close replica of the monomer band shape, but blue shifted with the 0-0 peak at 425 nm. This is observed both with 337 nm (Fig S46) (with an underlying monomer contribution) and 355 nm excitation, but critically not 437 nm (Fig 4f). This is a far clearer spectral contribution than the 420-425 nm shoulders we have previously observed. Moreover, using longer delay times of 10 ms and 50 ms, we see that this 425 nm band decays, estimated half-life around 10-20 ms, leaving very weak dimer emission at long times which, we assume, is remnant very slow long range TTA. This is the most unambiguous and clear spectral evidence of a monomolecular emission having very long lifetime, at 110 $\pm$ 20 meV above the monomer singlet emission, which we can only assign as inverted T_1 phosphorescence, with the important point that the predominant source of triplet states comes from $S_2 \rightarrow T_N$ ISC, as it is not observed when exciting the $S_0 \rightarrow S_1$ transition.

Lifetime measurements also exhibit a biexponential decay for toluene solution. Decay components and their respective contributions are concentration dependent (Figure S50). At 0.2 μ M (under 405 nm excitation) the decay comprises of τ_1 = 5.8 ns (88%) and τ_2 = 180.4 ns (12%) and, at 20 μ M, τ_1 = 13.0 ns (29%) and τ_2 = 191.7 ns (71%), further showing the impact of excimer formation and dynamic equilibrium between monomer and excimer to the decay. As with 2-MeTHF, lifetimes are weakly affected by the presence of oxygen in solution (Figure S51). As temperature decreases, a longer-lived decay is observed ($\tau_{80\text{ K}}$ = 3.29 μ s) (Fig S52), again associated with a non-thermally activated delayed fluorescence. At 80 K (Fig S53), prompt decay maintains a biexponential profile, where τ_1 = 27.6 ns (42%) and τ_2 = 124.9 ns (58%). Assuming excimer formation is heavily hindered by the frozen medium, decay components are tentatively attributed to dimer and monomer $S_0 \leftarrow S_1$ emission, respectively.

At a higher concentration of 20 μ M, we observe greater excimer contribution to the decay (Fig S54), with the emergence of dominant monomer emission around 1 μ s, which is observed for nearly 100 μ s at 80 K. The decay heat map shows these changes well (Fig S54c). At millisecond times, we see rather broad, weak emission peaking at 480 nm,

which we ascribe to dimer/aggregate delayed emission. At 20 μM , we do not see the 425 nm phosphorescence and believe that the increased dimer concentration effectively quenches monomer triplet states in competition with $T_1 \rightarrow S_1$ ISC. As we keep seeing throughout this study, excimers and dimers have a profound effect on the photophysics of HzTFEX₂ and, by inference, all heptazines, due to its planar structure.

Acetonitrile solution

Acetonitrile is the lowest polarizability solvent used and, potentially, the worst solvent used as far as solubility goes. Above the freezing point (Fig 5a-c) (200K as measured in the cryostat), both absorption and emission are very consistent with that observed in the other solvents, with monomer $S_0 \leftarrow S_1$ emission at 440 nm and dominant excimer emission at 480 nm. However, on freezing, the spectrum abruptly red shifts by 15 nm, with a huge increase in resolution and a large drop in intensity, some of which must be attributed to crazing of the solid solution. Monomer emission peaks at 455 nm, with the second vibronic now clearly resolved at 490 nm, along with 480 nm excimer and 520 nm dimer bands. These observations strongly indicate that energetic shifts of the monomer emission on freezing are polarizability dependent. Both $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ absorption band edges also red shift, matching that observed when monitoring excitation at 560 nm (Fig S55) i.e. monitoring pure dimer emission. The excitation spectrum monitored at 560 nm clearly shows dimer ground state absorption and the splitting of the feature at 410-430 nm, potentially indicating the presence of two dimer species.

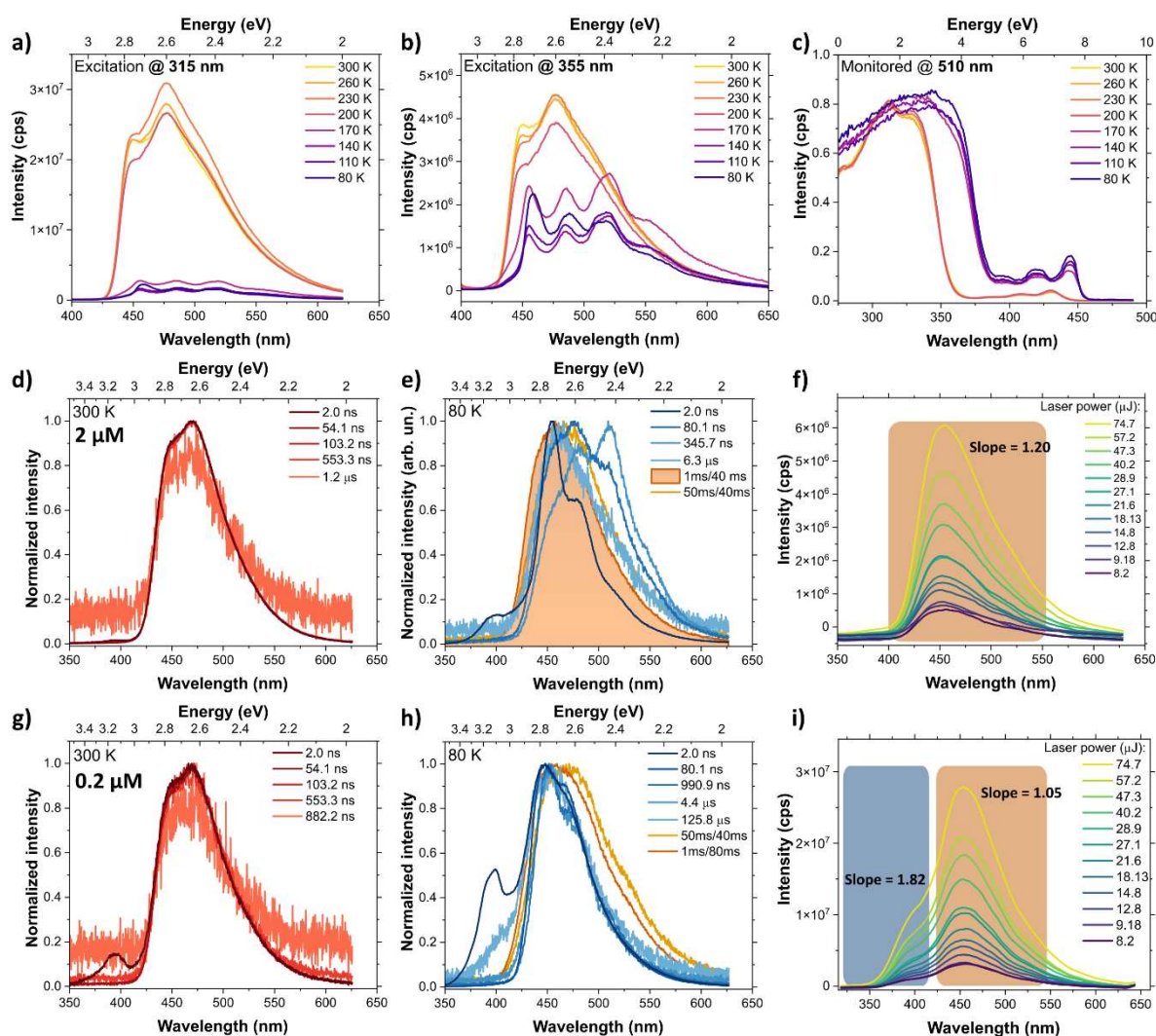


Fig 5. Photophysical characterization on acetonitrile solution. PL of H₂TFEX₂ in acetonitrile 2 μ M air saturated solution monitored in a range of temperatures. (a) λ_{ex} = 315 nm. (b) λ_{ex} = 355 nm. (c) Excitation profile monitoring emission at 510 nm in a range of temperatures. Signal was corrected by PL intensity. TRPL of H₂TFEX₂ in acetonitrile 2 μ M (d,e) and 0.2 μ M (g,h) air saturated solution monitored at (d,g) room temperature and (e,h) 80 K. λ_{ex} = 315 nm. (f) PL of H₂TFEX₂ in acetonitrile 2 μ M solution monitored at 80 K in a range of laser powers. DT = 10 μ s and integration time IT = 500 μ s. λ_{ex} = 337 nm. (i) PL of H₂TFEX₂ in acetonitrile 0.2 μ M solution monitored at 80 K in a range of laser powers. DT = 10 μ s and IT = 100 μ s. λ_{ex} = 337 nm. See SI for linear fit.

Time-resolved emission measured at room temperature (Fig 5d, g and S56) shows the characteristic mixed monomer and excimer emission. At 80 K, prompt emission is dominated by monomer singlet emission (DT = 2.0 ns) with a small dimer contribution. Excimer emission emerges from under the monomer curve after 20-40 ns, at both 2 μ M and 0.2 μ M concentration (Fig S57), although dimer emission is significantly less pronounced for 0.2 μ M. Monomer contribution is seen continuously from ns into the ms. We see the emergence of excimer and dimer emission at 480 nm and 520 nm, respectively, from under the monomer emission at DT = 345 ns, which decays by DT = 6 μ s, when pure monomer emission is observed again. We measured the power fluence

dependence at different time windows (Fig 5f and S58-62); at a delay and integration times of 10 μ s and 100 μ s, respectively, we obtain fluence dependences of 0.96, whereas a constant fluence dependence of 1.2 is obtained when IT is increased to 500 μ s. The fluence dependence at 0.2 μ M (at 80 K) is more instructive. Curves were collected with a DT of 10 μ s, integrating over 100 μ s three spectral regions under 337 nm excitation, $S_0 \rightarrow S_2$ (Fig 5i and S61). We observe a fluence dependence of 1.82 in the range 325 nm to 380 nm, coincident with the tail of the $S_0 \leftarrow S_2$ emission, which can only come from TTA, presumably in large aggregate sites or dense dimer regions. From 450 nm to 550 nm, the fluence dependence is 1.05 indicating that monomer, excimer and dimer delayed emission arises from monomolecular processes in this time window. Emission in the millisecond time range (Fig S62) gives a linear fluence dependency of 0.96.

Comparing the band shapes of prompt and delayed emission at 2 μ M and 0.2 μ M (Fig S63), we observe a large broadening of the prompt emission at the higher concentration, indicating the increased dimer content effecting both the red and blue edges of the emission band. At long times, when the dimer emission dominates, we observe the same broad emission spectrum. In the integrated spectra (DT = 1 ms, IT = 40 ms), we do observe a weak blue edge shoulder above the prompt emission, estimated peak position 420-425 nm, at both concentrations. The energy gap between the prompt and this phosphorescence is approximately 95 meV as measured by the band onsets.

Finally, we measured time-resolved emission exciting into the $S_0 \rightarrow S_1$ absorption peak, using 437 nm excitation. Despite maximum excitation power being moderate (20-30 μ J) and the HzTFEX₂ low absorption, we were able to obtain satisfactory time resolved emission (Fig S64). At 80 K, we observe very pure, narrow $S_0 \leftarrow S_1$ prompt emission, observed to around 1 μ s, with the slow emergence of underlying 480 nm excimer/dimer emission. We never observe any long-lived delayed emission at higher energy than the prompt emission in any time period. Given that we observe $S_0 \leftarrow S_2$ emission between 375 nm and 435 nm when exciting via the $S_0 \rightarrow S_2$ transition (337 nm), having a characteristic TTA fluence dependence, this verifies our assumption that the T_1 triplet population is primarily photocreated through excitation of an upper singlet state.

Discussion

It is clear from our measurements that the photophysics of HzTFEX₂ is far from simple and not intuitive. Given it is such a rigid, planar molecule, it should not be surprising that dimerization and aggregation play a dominant role. What is surprising is the very important role played by the S_2 state. The identified $S_0 \rightarrow S_1$ transition has a moderate extinction coefficient, $2130 \pm 50 \text{ M}^{-1}\text{cm}^{-1}$ indicative of a weak π - π^* transition through broken symmetry, in line with theory. The observed monotonic red shift with increasing solvent polarizability is consistent with previous observations in molecules possessing sp^2 hybridized nitrogen atoms within a conjugated structure²². Thus, we build a picture of HzTFEX₂ where the ground state is strongly localized due to the incorporation of the

localized nitrogen lone pair electrons in the π orbital, but the excited state is where a nitrogen lone pair electron is excited into the delocalized π^* orbital, changing the molecular polarizability, but not polarity, therefore environment polarizability interactions with HzTFEX₂ are important. In this view, we can understand the excited delocalized electron being highly decoupled from its localized hole, leading to very weak electron hole interactions, i.e. small electron exchange energies.

The overriding result from our work is that we believe we have enough evidence to state unambiguously that HzTFEX₂ yields long-lived T₁ phosphorescence, with a 0-0 peak at 425 nm and band shape nearly identical to monomer fluorescence, identifying the position of the monomeric HzTFEX₂ T₁ state and an inverted singlet triplet gap of 110±20 meV in frozen toluene at 2 μ M. It is important that the full conditions of the measurement are given, as we believe that this energy is sensitivity to the environment and excimer/dimer/aggregate content. Importantly, we observe a range of new results that support the strict criteria that need be met so that long-lived phosphorescence can occur from the lowest triplet excited state, energetically above the lowest singlet state, as depicted in Fig 6. We observe relatively strong anti-Kasha S₂ emission, indicating slow internal conversion from S₂ to S₁, because the S₂-S₁ energy gap is large, ca. 0.85 eV, and as the annulated heptazine core of HzTFEX₂ is rigid, crossing of the S₂ and S₁ energy surfaces will require large reorganization energy, but we find vibronic coupling is weak in HzTFEX₂ hindering this. Further, single crystal measurements indicate that the S₂ and S₁ transition dipole moments are orthogonal, so S₁ will be electronically decoupled from the higher state. Critically, we only observe T₁ phosphorescence when we excite into the S₂ state, indicating that ISC predominantly occurs in the upper S₂ singlet state. The relatively long S₂ residence time, >2 ns (giving rise to the observed S₀←S₂ emission) allows appreciable triplet formation in this case. Whereas exciting into S₁ yields no measurable phosphorescence and very weak delayed emission, clearly showing that endothermic S₁→T₁ (and hence T₁→S₁) ISC are highly suppressed, due to weak vibronic coupling. Following El-Sayed's rule that orbital angular momentum must change for SOC to cause ISC, both S₁→T₁ and T₁→S₁ ISC in HzTFEX₂ are forbidden. However, as we have previously shown for TADF materials, vibronic coupling between T₁ and T₂ can mediate SOC and allow ISC between degenerate S₁ and T₁ states^{33–35}. For HzTFEX₂, T₂ is calculated to be 0.65 eV above T₁ (see SI section 6), an energetic gap too large to effectively mix these states by vibronic coupling, and so the TADF spin-vibronic coupling mechanism will also not contribute to S₁ ↔ T₁ ISC in HzTFEX₂. Therefore, only when we excite S₀→S₂ do we observe long lived emission that is bluer than prompt monomer emission. Thus, appreciable triplet population is only formed through efficient S₂→T_N ISC. Following the calculations of Dinkelbach⁷ this would be S₂-T₅, for example.

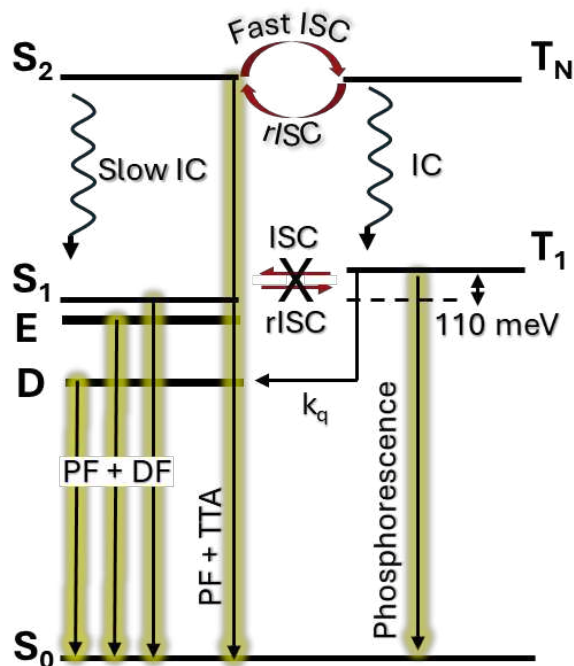


Fig 6. Summary of photophysical processes of HzTFEX₂. Jablonski-Perrin diagram depicting the relevant excited-state mechanism of monomeric and non-monomeric species of HzTFEX₂. $\Delta E_{S_1-T_1}$ is given as measurement in toluene 2 μ M solution. E represents excimer energy levels; D represents dimer energy levels and k_q is the rate of dynamic quenching.

Emission is almost always a convolution of a monomeric singlet contribution at 450-460 nm (dependent on environment), excimer at 480 nm (in fluid solution) and dimer emission at 520 nm, making it very difficult to measure the properties of the pure monomeric species. The excimer/dimer states are clearly resolved in single crystal and powder emission spectra. Typically, the excimer/dimer emission dominates, leaving the monomer emission appearing to be a weak blue shoulder on the total emission band. In several cases this has been misidentified as $S_0 \leftarrow T_1$ phosphorescence.

We conclude that emission lifetimes in solution are complex and dynamic, governed by a monomer-excimer equilibrium. In dilute 2-MeTHF solution, we measure a PLQY at room temperature of 0.42 ± 0.05 and observe high excimer/dimer content in the emission, however, on freezing, the spectra changes abruptly, consisting of near pure, blue shifted (435 nm) prompt monomer emission, with very low excimer and dimer content. The energy shift happens due to polarizability change, not because phosphorescence suddenly becomes dominant. We estimate that the PLQY reaches near unity at 80 K, and the significant increase, compared to RT, is due to suppression of excimer formation. This points to negligible excited state loss by internal conversion and non-radiative decay such as ISC, supporting our point that vibronic coupling in HzTFEX₂ is very ineffective, especially in the S₁ and T₁ manifolds, again supporting the requirement that $T_1 \rightarrow S_1$ ISC is negligible so that long lived phosphorescence from T₁ can be observed. It also enables long lived collisional TTA to occur in fluid solution, along with aggregate TTA in frozen solution and film. We also observe $S_0 \leftarrow S_2$ emission for 5 decades after pulsed

photoexcitation, having a characteristic quadratic power fluence dependency of TTA, indicating that $2x E_{T_1} > S_2$ and that $T_N \rightarrow S_2$ reverse ISC is efficient. Suppressed excimer formation in frozen solvent also leads to longer monomer lifetime, of around 100 ns (solvent dependent) and with near unity PLQY this represents the $S_0 \leftarrow S_1$ radiative emission decay rate. In poor solvents, with high dimer population, collisional and or FRET energy transfer will quench the long-lived monomer singlet states as well.

At room temperature, we never observed emission after around 1 μ s, whereas at 80 K, we can measure emission beyond 80 ms. These observations imply that, at 80 K, all vibrationally coupled non-radiative processes are greatly slowed down or fully suppressed. Low-temperature delayed emission is monomolecular, coming from the triplet population initially generated in S_2 , with around half the intensity observed in fluid solution. The monomolecular delayed emission is observed equally at 80 K and 20 K and so must signify very slow exothermic $T_1 \rightarrow S_1$ ISC, not a thermally activated type mechanism.

We do observe direct evidence for phosphorescence at higher energy than the monomer $S_0 \leftarrow S_1$ transition, in a range of different environments at low temperature, from as early as 100 μ s and up to 10 ms. A compendium of such spectra is given in Fig S65. We consistently see a shoulder or more resolved band with a 0-0 peak at 425 nm, with the proviso that we excite through the $S_0 \rightarrow S_2$ transition. A similar emission in frozen solution has been reported previously for a carbazole-substituted hexaazaphenylene³⁶.

The most definitive phosphorescence spectrum we have recorded is in 2 μ M frozen toluene solution (Fig 4e), but it still contains a contribution from very long-lived dimer emission (most likely delayed emission arising from TTA within aggregates, not isolated dimers), causing an up-lift of the 0-1 and 0-2 vibronic transitions. We believe that the phosphorescence and fluorescence have near identical spectral band shapes as would be expected by nearly degenerate orbitals. We estimate a T_1 lifetime in the order of 10-20 ms, and an inverted energy gap $\Delta E_{T_1-S_1}$ of 110 ± 20 meV in frozen toluene at 2 μ M. It is important here to stress the full conditions of the measurement given the obvious sensitivity of HzTFEX₂ to environment and excimer/dimer/aggregate content. This value is similar to the 47 meV T_1-S_1 inverted gap reported by Wilson et al¹³ in 1,3,4,6,9b-pentaazaphenylene, using high-resolution cryogenic anion photoelectron spectroscopy. Dinkelbach et al.⁷ show calculations for a substituted heptazine where the $S_1 \rightarrow T_1$ rISC rate depends strongly on the magnitude of the inverted $S_1 - T_1$ gap. Beyond ca. 90 meV, it is effectively zero, which sits well with our optical measurements, so that exciting the $S_0 \rightarrow S_1$ transition leads to very low triplet generation so little or no DF and phosphorescence.

Given the very long lifetime of the monomer triplet, we believe that the triplets can be quenched by slow long range energy transfer to dimers even in frozen solution and guest-host film, as the phosphorescence intensity is highly dependent on dimer content. Very

dilute conditions are required, which obviously makes measurements difficult. Further, with the contribution of delayed emission from the dimers, one has to take account of the wings of the dimer emission that can be stronger than gaussian and can extend beyond the on-set of the monomer emission. This combined with the inevitable noise on the very weak signals can mask the phosphorescence.

For a 2 μ M acetonitrile solution, DF measured at TD = 10 μ s /IT = 500 μ s yields a mixed fluence slope of 1.19, but at 10 μ s/100 μ s it is 1, indicating that TTA is very slow and inefficient. At DT > 1 ms, the delayed spectra is dominantly dimer, but still bears a monomolecular power dependence. Here we are monitoring very weak emission, approximately 10^6 less intense than early time delayed emission. A monomolecular process driving this is much harder to understand. The obvious one is phosphorescence, but the emission peaks at 470 nm and the band is much broader than that observed at early times, which could imply a large degree of disorder in the dimer/aggregate sizes and configurations. At 470 nm the emission is though slightly bluer than dimer at room temperature (480 nm), which might imply inversion of the dimer lowest energy singlet and triplet states as well. Ehrmaier et al.⁵ have calculated the energy states for heptazine dimers, finding inversion, which would support this idea.

Finally, we return to room temperature behaviour. We never observe emission beyond around 1 to 2 μ s, no delayed emission, TTA or phosphorescence, just monomolecular decay of the monomer and excimer species. Very different behaviour to that seen below 80 K. We believe that this implies that, at high temperature, vibrational coupling is active to such a degree that $S_1 \rightleftharpoons T_1$ ISC is efficient, especially exothermic $T_1 \rightarrow S_1$ ISC, so that any triplet population in T_1 rapidly crosses to the lower singlet S_1 state. With an inverted gap of over 100 meV, the endothermic $S_1 \rightarrow T_1$ ISC could either be ineffective or fully out competed by the much faster $T_1 \rightarrow S_1$ process. Thus, in the context of an OLED operating at or more typically above room temperature, triplet harvesting, the conversion of triplet excitons, formed during charge recombination, to singlets proceeds rapidly. In comparison to a typical Ir complex emitter of 2 μ s lifetime, the heptazine decays at a faster rate. Thus, HzTFEX₂ based devices can attain external quantum efficiencies of 17%¹⁹. However, as we have shown, at doping levels above even 0.1% excimers dominate, with OLED peak emission at 480 nm¹⁹, and so potentially triplet harvesting could occur through the excimer states, which may or may not themselves be inverted. We have observed that the PLQY of excimer dominated solutions is lower than predominantly monomer frozen solutions which may be the reason why HzTFEX₂ devices only reach 17% EQE¹⁴, opening the possibility to designing new heptazines with side groups that hinder excimer formation, which could achieve much higher EQE values.

Conclusions

The photophysics of HzTFEX₂ is invariably complicated, displaying many counterintuitive processes. It is dominated by excimers and dimers in solution and dimers and aggregates in solid state. We believe our measurements gives enough evidence for S₁ T₁ inversion, with an inverted singlet triplet energy gap of 110±20 meV in frozen toluene at 2 μM. We give clear insight as to how it is physically possible for long-lived phosphorescence to occur from a triplet state higher in energy than its singlet counterpart, using a wide range of photophysical measurements. The role of the second excited singlet state is shown to be crucial in this, especially in generating triplets after photoexcitation, as we observe that S₁↔T₁ ISC is highly inefficient. This though is not bad news for application of HzTFEX₂ as an efficient triplet harvesting emitter in OLEDs however, as we have shown that at room temperature vibronic coupling becomes active, giving rise to fast exothermic T₁→S₁ ISC and potentially efficient triplet harvesting. At typical 10 wt% HzTFEX₂ loadings, excimers will dominate, giving rise to moderate emission efficiency, limiting devices to around 17% EQE to date. Thus, more work now is needed to understand how heptazines behave within a typical OLED emission layer environment and how excimer formation can be controlled, leading to higher device efficiencies.

Methods

Sample preparation

Guest-host films were fabricated through drop-cast method onto quartz substrates. A 100 mg/mL solution was used for the host, and the adequate amount of guest (HzTFEX₂) was added to reach the desire doping concentration. Solutions in toluene, 2-methyltetrahydrofuran (2-MeTHF), acetonitrile (MeCN) and methylcyclohexane (MCH) were used for the investigations. High purity, spectroscopic grade solvents were purchased from Romil and used without further purification. Low concentrations were employed to avoid aggravation of the presence of dimers in solution. Additionally, degassing was done by bubbling the solution with argon for 20 minutes to avoid aggregation.

Single crystal X-ray diffraction

The X-ray single crystal data of HzTFEX₂ has been collected at a temperature of 120.0(2) K using MoKα radiation (λ =0.71073Å) on a Bruker D8 Venture with a Photon III MM C7 CPAD detector, IμS-III-microsource, focusing mirrors diffractometer equipped with a Cryostream (Oxford Cryosystems 700+) open-flow nitrogen cryostat. Using APEX5 software³⁷, intensities were integrated in SAINTS³⁸ and absorption corrections based on equivalent reflections were applied using SADABS³⁹. The structure was solved using ShelXT⁴⁰ structure solution program using Intrinsic Phasing and refined by full matrix least squares against F² in ShelXL⁴¹ using Olex2⁴². All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystal data and parameters of refinement are

listed in Table S1. Crystallographic data for the structures has been deposited with the Cambridge Crystallographic Data Centre with deposition number CCDC-2551605. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Steady state measurements

A Jobin Yvon Horiba Fluorolog (double-double) spectrofluorometer and a Shimadzu UV-vis-NIR 3600 spectrophotometer were used for emission and absorption measurements, respectively. The relative PLQY of HzTFEX₂ in 2-MeTHF (2 μ M) at room temperature was measured employing diphenylanthracene (DPA) as a standard and following literature procedure⁴³. For 80 K, PL was acquired under identical conditions, at room temperature and 80 K. Emission intensity was converted to quantum efficiency by considering the integrated PL (300 K and 80 K) and relating it to the PLQY previously measured at room temperature. 2-MeTHF was used since it forms a glass at low temperatures, avoiding losses due to scattering.

Time-resolved measurements

The time-resolved spectra were obtained using a Stanford Computer Optics 4Picos gated iCCD camera (250–950 nm) with sub-nanosecond resolution and spectrograph equipped with 300 lines/mm grating, 500 nm blaze wavelength system. Excitation was from the 3rd harmonic of an EKSPLA 200 ps Nd:YAG (10 Hz repetition rate laser), from a Lasertechnik Berlin nitrogen laser (30 Hz repetition rate) laser or from a coumarin 440 dual pass dye laser, pumped at 355 nm from the Nd:YAG laser. Time-resolved measurements were made using a variable CCD gate and delay times relative to the laser trigger. TCSPC measurements were recorded with a Horiba DeltaFlex system using a Horiba DeltaDiode (405 nm) and SpectraLED (330 nm) as light sources. For vacuum and/or cryogenic temperature measurements the samples were placed in a cryostat (Janis Research VNF-100) and cooled down by nitrogen flow. A helium-closed cycle cryopump equipped with optical windows, Si thermodiode, and sample mount, attached directly to the cold head was used for measurements at 20 K. All spectral onset energies were corrected using the Jacobian conversion of wavelengths to energies. Additionally, it was found that steady time and time-resolved curves slightly shifted, to around 5 nm. (Fig S67).

Theoretical calculations

The calculations of the energy levels and molecular orbitals for the main transitions of HzTFEX₂ in the singlet and triplet manifolds were performed in vacuum using time-dependent density functional theory (TDDFT) with the LC-BLYP functional and the 6-31+G(d) basis set within the Tamm–Dancoff approximation. The range-separation parameter of the LC-BLYP functional was set to 0.18 bohr⁻¹, following a previous study on

H₂TFEX₂¹⁹, to balance the Hartree–Fock exchange with the DFT exchange. All calculations were carried out using the Gaussian 16 Rev C.01 program.

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Author contributions

H.M.S and A.M. conceived the study. N.A. provided HzTFEX₂ and performed theoretical calculations. C.F., H.M.S and C.R. performed steady state and time-resolved photophysical measurements. C.R. grew single crystals. C.F., H.M.S., C.R., N.A and A.M. analysed and discussed the data. A.M. wrote the manuscript with input from all authors.

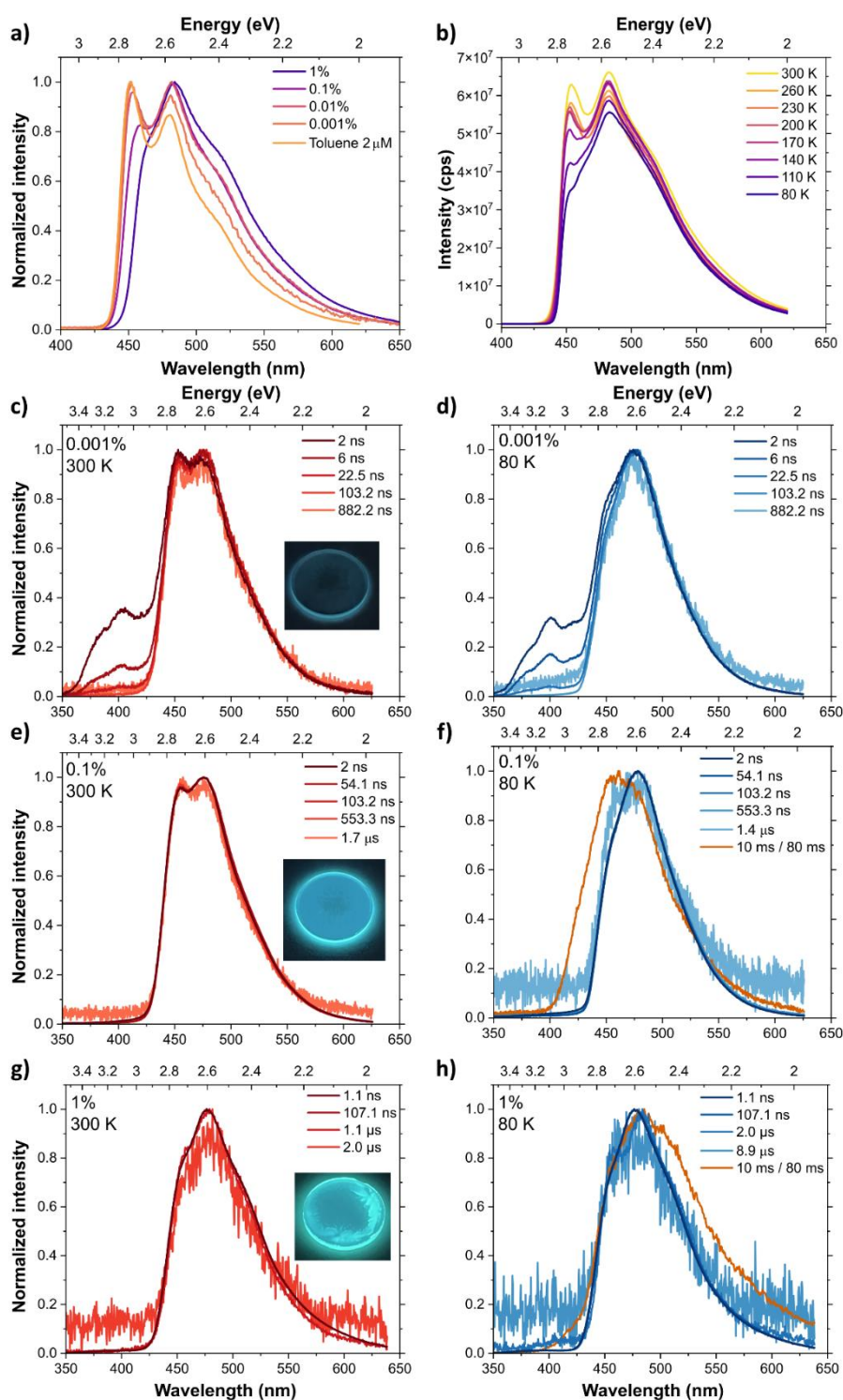
Competing interests

The authors declare no competing interests.

Additional information

CIF files for HzTFEX₂ been deposited with the Cambridge Structural Database, CCDC 2551605. Supplementary information is provided.

Extended data



Extended Data Fig 1. Investigation of photoluminescence of Zeonex host-guest system. (a) Normalized PL of H₂TFEX₂ doped into Zeonex guest-host films in a range of concentrations monitored at room temperature. PL of 2 μ M toluene solution was added for comparison. λ_{ex} = 350 nm. (b) PL of H₂TFEX₂ doped into Zeonex guest-host films at 0.1% wt/wt monitored in a range of temperatures. λ_{ex} = 355 nm. TRPL of H₂TFEX₂ doped into Zeonex guest-host films at 0.001% (c, d), 0.1% (e, f) and (g, h) 1% at room temperature and 80 K. λ_{ex} = 355 nm. Inset shows the luminescence of the films under 365 nm lamp.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

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