The Photophysics of an Asymmetric Donor-Acceptor-Donor' TADF Molecule and Reinterpretation of Aggregation Induced TADF Emission in these Materials.

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Abstract

We report an in-depth photophysical investigation of an asymmetric Donor-Acceptor-Donor' (D-A-D') thermally activated delayed fluorescence (TADF) molecule (4-(9H-carbazol-9-yl)phenyl)(4-(10H-phenothiazin-10-yl)phenyl)sulfone and compare its photophysical properties to the parent symmetric D-A-D and D'-A-D' molecules. These D-A-D type small molecules all show strong TADF. The work reveals how the relative orientations of D-A (D'-A) moieties favour reverse intersystem crossing (rISC) by forming stable charge transfer (CT) states. The key requirement for the efficient TADF emitters is to achieve a very small CT-local triplet state energy splitting, which is shown to be complex in the asymmetric molecule. Throughout the investigations, we show that in the asymmetric D-A-D' system, even though E_{CT} (D-A) > E_{CT} (D'-A), no evidence of energy transfer from D-A to A-D' is observed, nor from excited D to D'. This is ascribed to the near orthogonality of the D and D' units and the very strong decoupling of the electrons on the D and A in the CT state. In addition, the possibility of aggregation induced TADF (AI-TADF) is examined in these particular molecules and shown to be a manifestation of solvatochromism in these materials.

1. Introduction

The growing applications in display and illumination technologies [1–3] makes organic light emitting diodes (OLEDs) a very attractive field of research. A main objective is to improve the performance of OLEDs by achieving high quantum efficiency (QE), which is associated with the quantity of emissive singlet states generated during charge recombination. According to spin statistics,[4] emissive singlets and non-emissive triplet states are formed in the ratio of 1:3, which

imposes a serious 25% limitation to the internal quantum efficiency of OLEDs. For this reason, several approaches have been developed to overcome this limitation, either using heavy metal complexes for phosphorescence emitters[5] or designing novel small-molecule or polymeric organic emitters to convert non-emissive triplets to emissive singlets *via* triplet-triplet annihilation (TTA) or thermally activated delayed fluorescence (TADF); the latter enables near 100% internal efficiency in OLEDs.[6,7] Recently, donor-acceptor (D-A) type emitters have been introduced as promising TADF materials for OLEDs.[8–12] These emitters have very small CT-triplet energy gaps (ΔE_{ST}) due to their intrinsic intramolecular charge transfer (CT) excited states.[13–15]

Photophysical measurements are ideal for studying the mechanism of reverse intersystem crossing (rISC) and TADF in these CT molecules. Following optical excitation, the molecules undergo internal electron transfer from a $D^{\delta+}$ to an $A^{\delta-}$ moiety, which is usually accompanied by conformational changes to form a new stabilized dipolar state, a charge transfer state or exciplex (where D and A are not chemically bound). Indeed, this state can be formed directly on excitation, or it may sequentially form *via* locally excited (excitonic) states by excited state electron transfer. These newly formed states have their own photophycial properties and spatial molecular conformations, arising from twisting, bending or planarization about the D-A bond in the excited state, and can be stabilized by solvent polarity and temperature.[16,17] The importance of the CT state comes from its active role in the interconversion of triplets *via* a vibronic coupling reverse intersystem crossing mechanism; concomitantly TADF arises with high efficiency.[18–20] Because of this complex mechanism, there exist two fundamental requirements to achieve high efficiency from TADF: i) the ΔE_{ST} between ^{1}CT and ^{3}CT should be minimised and near resonant with a local (D or A) triplet state [13,20] and ii) non-radiative decays that occur in all

excited states should be minimised.[21,22] However, it is not that easy to design efficient TADF molecules due to the problems arising from energy level orderings, splittings and vibronic couplings.[20,22,23] Recent reports have focused on understanding how the efficiency of rISC (and hence TADF) is affected by the ordering of energy levels in new emitters,[13,20,22,24] where the near-orthogonal orientation of D-A-D units determine the final molecular configurations that favour the formation of emissive singlet-CT (^{1}CT) and triplet-CT (^{3}CT) states with vanishing ΔE_{ST}. Indeed, this then leads to efficient rISC, and TADF. The very small ΔE_{ST} enables efficient triplet to singlet conversion. This is because electronic coupling between energetically close ^{1}CT, ^{3}CT and locally excited (^{3}LE-triplet) states result in significant spin-orbit interaction[13,22] which is mediated by second-order vibronic coupling (of ^{3}CT and ^{3}LE) to enable spin conversion of the triplet states back to the ^{1}CT state, thereby enabling TADF emission. The critical point for the second-order vibrational coupling model of rISC is energy ordering, which is associated with the conformational changes of molecular structures.[13,20] However, it must be noted that the first order spin-orbit coupling (SOC) is forbidden between ^{1}CT and ^{3}CT states.[25]

Here we investigate the excited-state dynamics in donor-acceptor-donor (D-A-D) TADF emitters which were designed with the same central electron acceptor (diphenylsulfone, SF) moiety and two electron-donating units consisting of carbazole (C) (symmetric, SF2C) or phenothiazine (P) (symmetric, SF2P) units, and an asymmetric SFPC molecule, containing one phenothiazine and one carbazole units. We particularly focus on the photophysics of the asymmetric SFPC molecule, as it has been reported to be one of the most efficient TADF emitters in the literature.[26,27] In addition, two of the materials, SFPC and SF2P, were reported to give "aggregation induced" TADF emission from their aggregated states, whereas SF2C was considered as a "normal" TADF emitter, showing aggregation caused quenching.[26] To

understand the photophysics of these TADF systems, we made in-depth investigations in very dilute solutions and reveal new findings that shed light on the actual nature of the reported "aggregation induced" TADF phenomena, as well as understanding the effect of having mixed donors in an asymmetric D-A-D' molecule.

2. Experimental

During the all experiments very dilute solutions were prepared, which were in the range of $7 \times 10^{-5} \sim 4 \times 10^{-6}$ M. Absorption and emission spectra were collected using UV-3600 double beam spectrometer (Shimadzu), and Fluoromax amd Fluorolog fluorescence spectrometers (Jobin Yvon). All solvatochromic measurements were taken in air-saturated solutions using with 1cm depth quartz cuvvettes, and at least 3 freeze-thaw cycles have been done for degassing the solutions, using a long necked quartz degassing cuvette and the liquid nitrogen cryostat (Janis Research). Time-resolved nanosecond gated luminescence measurements were performed using a high energy pulsed Nd:YAG laser excitation (SL312, EKSPLA) emitting two harmonics at 2.33 eV (532 nm) and 3.49 eV (355 nm). The pulse duration is approximately 150 ps; more details about the nanosecond time-resolved spectroscopy can be found elsewhere. [30] The energy per pulse was chosen around 100 μJ.

3. Results and Discussion

For the symmetric SF2C and SF2P molecules (see Fig. 1 a. and b.), the emission spectra appear broad and featureless. For SF2C, the CT band shows very little solvatochromic shift with the emission peaking at the same wavelength, *ca.* 407 nm, in both chloroform and 2-methyltetrahydrofuran (2-MeTHF), whereas SF2P shows a shift from 540 to 555 nm on

changing from toluene to 2-MeTHF. The relative Stokes shift is larger in SF2P than in SF2C, indicating stronger CT in the former, which can be attributed to the spatial orientation of phenothiazine unit. In SF2P, the nitrogen lone pair shows strong localization, which results in strong decoupling between donor and acceptor units (see Fig. S1 in SI). This is confirmed by the nearly orthogonal orientations of HOMO-LUMO orbitals on the donor and acceptor units,respectively,[19] which is the case for the geometry of D-A units of SF2P, showing equatorial-equatorial conformations.[26,28] In zeonex solid host matrix, SF2C displays a much narrower emission band with less Gaussian line shape, it peaks at much lower wavelength, but the onset of the band is very similar to the emission in 2-MeTHF. This indicates a weaker CT character in zeonex with the emission having an increased amount of local (singlet) excited state character. The emission of SF2P in zeonex is red shifted compared to that in toluene, indicative of a restricted spatial environment, but still the emission is Gaussian and strongly CT in character. The solvatochromic shift is commonly encountered in D-A-D type molecules, where the change in relative orientations of D-A moieties, or shielding of the Coulomb exchange between the charges on the D and A units, stabilizes the intramolecular interactions and red shifts the excited charge transfer state to lower energy.[17,22] These results indicate that SF2C behaves rather differently than most other reported D-A molecules because the D-A torsion angle id already large (70 to $>85^0$) in these D-A-D moelcules.[18] If ΔE_{ST} becomes small enough, a significant proportion of the emission arises from the CT states as delayed fluorescence (DF). The emission of SF2C and SF2P arises solely from [1]CT states even in the solid state (either as the pure sample or in zeonex isolated films) and in a variety of solutions at room temperature (RT). The energies of the local triplet states of these molecules determined from millisecond delayed emission measurements, see Fig. S2 in supporting information (SI), are 2.47 ± 0.01 eV

for SF2P and 2.99 ± 0.01 eV for SF2C, giving a ^{1}CT- ^{3}LE energy gap (ΔE_{ST} =0.15 ± 0.01 eV in toluene) for SF2P, compared to (ΔE_{ST} =0.28 ± 0.03 eV in chlorobenzene) for SF2C. In both systems, the DF is strongly oxygen dependent (fully quenched in the presence of oxygen) and shows unvarying spectral shape with time (see Fig. S3 in SI), confirming that the prompt and delayed fluorescence always arise from the same ^{1}CT states and no spectral relaxation occurs at late delayed times.

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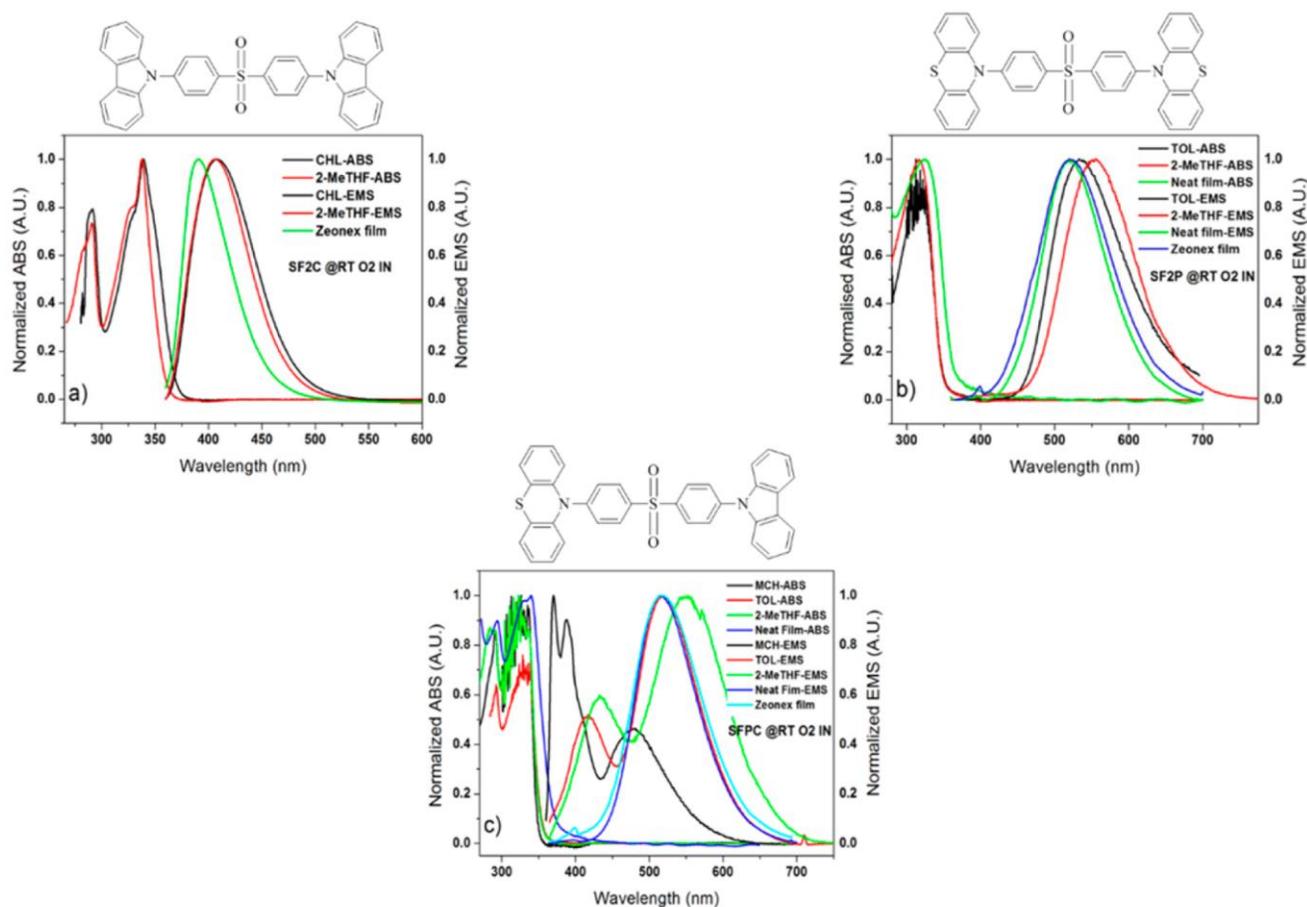
Figure 1. Normalized room temperature absorption (ABS) and emission (EMS) spectra of molecules; **a)** SF2C **b)** SF2P and **c)** SFPC, in a variety of solvents: methylcyclohexane (MCH), toluene (TOL), chlorobenzene (CHL) and 2-methyltetrahydrofuran (2-MeTHF)), neat and zeonex (5% wt/wt) films. The chemical structures of the molecules are given on top of the each figure.

The X-ray crystal structures of SF2C and SF2P have been reported.[26] The near-planar conformation of D and A in SF2C has the effect of making the CT state in SF2C rather weak with little solvent stabilization and almost pure ^{1}LE emission in non-polar media is observed. However, in SF2P, with a near-orthogonal relative orientation of D-A units, the CT state is much stronger, even in non-polar media and undergoes far greater solvent stabilization in polar media.

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However, measurements of SF2C in frozen 2-MeTHF solution at 80 K, show dominant structured prompt ^{1}LE donor emission with no prompt or delayed ^{1}CT emission (see Fig. S4a. in SI). This is not typical behaviour for D-A-D systems.[18] At later times, it is possible to detect a small emission from a donor dimer state (emission peak at 475 nm compared to 425 nm for the SF-C Ct state),[29] in keeping with the X-ray crystal structure of SF2C (see S1 in SI) [26] and then in the millisecond regime, well-structured D phosphorescence is observed. This is again consistent with the lack of any CT states that could mediate rISC. In the symmetric SF2C, high polarity media would seem to stabilize the CT state in favour of the more conjugated, planar local states in low polarity. For the carbazole donor, which is weak, the stabilization of the CT state requires a polar environment otherwise conjugation with the acceptor wins out and reduces the torsion angle, yielding a strongly local done character excitation. This is because the nitrogen lone pairs of the carbazole are conjugated into the carbazole backbone.[17] These findings also better explain the previous report,[26] which found that on addition of water to THF the emission from the SF2C red shifted in accord with increasing solvent polarity, but also that the intensity of emission drastically reduced. At 90% water content, the SF2C has presumably precipitated out of solution and weak emission at 420 nm is observed again from the suspension of SF2C.[26]

For, SF2P in 2-MeTHF (see Fig. S4b in SI), the DF is strongly red shifted, and electron transfer is slowed such that over the first 5-6 ns, the ^{1}LE emission is observed along with the grow-in of the ^{1}CT emission. The intensity of DF only gradually decreased with temperature, but completely disappeared when the solvent is totally frozen (at 80 K). This indicates that at 80 K in rigid frozen solution, the vibrational motion required for vibronic coupling is frozen out and rISC becomes too slow to contribute any DF. In keeping with the near-orthogonal orientation of the D and A units of SF2P (see Fig. S1 in SI), the CT state is always stabilized. As observed with a

related D-A-D emitter with a central dibenzothiophene-*S-S*-dioxide core (DPTZ-DBTO2) in highly polar environments, the CT state of SF2P is stabilized so much that the [1]CT emission lifetime increases greatly and is out-competed by non-radiative decay.[22] The DF is also very inefficient because the ΔE_{ST} gap grows too big to sustain sufficiently fast rISC.[22]Again, in the previous report,[26] as water is added to a THF solution of SF2P, the solvent polarity increases and a red shift of emission with concomitant decrease in intensity is observed. Only at 90% water fraction does a strong PL signal return but with a large blue shift indicating that this is from aggregates that have precipitated. Our new results show that this effect is not aggregation induced emission (AIE) but is a manifestation of strong solvatochromism on a highly charge-separated excited state, and once the SF2P precipitates, the solid is a much less polar environment (than the dissolved molecule experiences in the polar solvent) as seen by the large blue shift of the emission, accompanied by increased emission on precipitation. AIE is a different mechanism whereby a molecular motion is frozen upon precipitation such that the rate of non-radiative internal conversion charges greatly. This causes large changes in emission intensity but no shift of the emission.

In the light of the above understanding of the basic properties of the symmetric D-A-D parent molecules, we now turn to the more complex asymmetric SFPC molecule (see Fig. 1 c.). The normalized absorption and emission spectra of SFPC clearly reflect the CT characteristics of both parent molecules (SF2C and SF2P). The structured absorption spectrum is a sum of the absorption spectra of each D and A component, which can be attributed to the decoupled nature of donor and acceptor (for both carbazole and phenothiazine donors).[27] Furthermore, the emission of SFPC shows dual Gaussian band shaped emission, where the origin of broad unstructured "blue-emission" is attributed to the [1]CT state of the SF-C A-D pair, which clearly

undergoes a red shift with increasing solvent polarity. The "green-emission" is attributed to [1]CT state emission from the SF-P A-D pair, and behaves like its parent SF2P (Fig. 1b). Both bands of the dual emission show positive solvatochromism, and correspond to emitted wavelength contributions of both the symmetrical parent molecules. However, in non-polar MCH solution, the SF-C emission appears well-resolved (even in different MCH concentrations, see Fig. S5 in SI) with greater intensity than the SF-P [1]CT emission. This well-resolved emission in SF-C is attributed to pure carbazole donor emission, [1]LE, where the onset value is determined as 3.40 ± 0.04 eV at RT. This result indicates that the radiative recombination from the [1]LE locally excited singlet state of carbazole competes with electron transfer that creates the SF-C [1]CT state, confirming the weak electronic coupling between the [1]LE and [1]CT states of the more planar conformation of the D and A units (reduced dihedral angle) in the SF-C system and the lack of stabilization of the [1]CT excited state. This further confirms the observations of the parent SF2C emission in 2-MeTHF. For SFPC, with increasing solvent polarity, the structured blue emission (in MCH) red shifts and gains a Gaussian band shape, peaking at *ca.* 417 nm in toluene and *ca.* 433 nm in 2-MeTHF, as well as a significantly decreasing in intensity. These data clearly indicate the stabilization of the CT state on the SF-C unit in the SFPC molecule with increasing polarity. This effect is less obvious in the parent SF2C, which we ascribe to stronger conjugation in the more planar SF2C molecule, as compared to the near-planar orthogonally twisted molecular geometry of the SFPC (see S1 in SI). In neat and isolated (zeonex 5% wt/wt) films the [1]CT-SF-P emission appears at same wavelength as in toluene, but no SF-C [1]CT or carbazole [1]LE emission is observed. This implies that carbazole moiety cannot rotate in the host matrix to stabilize the CT state, so all excitation goes into forming [1]CT-SF-P states directly, or all carbazole [1]LE energy funnels into the phenothiazine moiety.

The contribution of triplets to the overall SFPC emission was determined by comparing the emission intensity in aerated and non-aerated toluene (TOL) solutions (see Fig. S6 in SI), where the dual emission peaks of SFPC perfectly match with the ^{1}CT state of SF2C (blue-emission) and ^{1}CT state of SF2P (green-emission). Once the oxygen is removed from SFPC, the change in intensity of blue-emission is relatively weak compared with the significant change in intensity of green-emission, also resulting in a significant jump in quantum yield of the system, from 28.8% to 99.2% in solution, and up to 93.3% in the solid state.[26] This indicates a more efficient triplet harvesting mechanism in the SF-P arm, compared to the SF-C arm, in agreement with the different CT-^{3}LE gaps of the two sub-units.

To obtain a better understanding of the relationships between the molecular structures and emissive states we used time-resolved spectroscopy,[30] where the nature of complex emissive states of SFPC can be determined more accurately. First, the fluorescence decay was studied in slightly polar toluene (TOL) solution (ε = 2.38, ground state dipole moment μ=0.43D), noting that the dielectric coefficient of toluene increases as temperature decreases towards it's freezing point.[31] In Fig. 2a, where the prompt fluorescence (PF) decay followed by well-defined long-lived delayed fluorescence (DF) decay is observed. The intensity of the DF is clearly higher at high temperatures, supporting an active TADF mechanism, and follows an exponential decay until the solvent is totally frozen at 120 K. At 120 K, the decay follows a power law (t^{-m}) with m approaching a value of 1 (see inserted plot in Fig. 2a at 120 K), indicative of an inhomogeneous system, i.e. a strong dispersion of the rISC and decay rates in the system. The decay curves of SFPC show clearly three distinct regions, delineated by two well-defined crossing points: 74 ns and 44.6 μs (vertical dashed lines in Fig. 2a). The decay below 74 ns is assigned as prompt emission (^{1}CT→S$_0$), with the blue, 420 nm, ^{1}CT-carbazole state decaying

rapidly in a few nanosecond (~5 ns) whereas the [1]CT-phenothiazine state remains the dominant emissive state over the first 50-70 ns (see initial delay times in Fig. 2 b). Thereafter, between 74 ns – 1.2 µs, pure SF-P DF dominates the decay curve and this time frame is assigned as "Region 1" in Fig. 2a, where a significant triplet harvesting cycle occurs between [3]LE-phenothiazine and SF-P [1]CT states. Both the prompt [1]CT emission and DF are temperature dependent - the DF as expected, but the PF also, where we observe stronger but faster [1]CT decay at high temperature, in accordance with the vibronic coupling theory where both ISC and rISC rates increase at higher temperature (and small ΔE_{ST}).[19] From the time evolution of the emission spectra at 295 K, at early times (1.44 ns to 21.04 ns), the SF-C and the SF-P emission both arise as a dual emission, but after 35.74 ns delay time only the SF-P state emits (*ca.* 527 nm) which persists until 398.1 µs delay time (Fig. 2b). Indeed, the interconversion of triplets *via* the rISC mechanism is highly promoted between vibronically coupled [3]LE and [1]CT-phenothiazine states (the ΔE_{ST} is very small at 295 K in Fig. 2c). However, the states decouple with reduced temperature and as the ΔE_{ST} is increasing, i.e. the DF peaks at 580 nm at 120 K (Fig. 2c). This is due to a solvent effect, where toluene becomes more polar as it is cools. Therefore, with increasing polarity the SF-P [1]CT emission red shifts, but the intensity decreases significantly as ΔE_{ST} increases. Consequently, at 295 K ΔE_{ST} is very small and we would expect DF to be strong; however, the changing toluene polarity increases the gap and decreases DF, so at 120 K the gap is so large that little DF is observed.
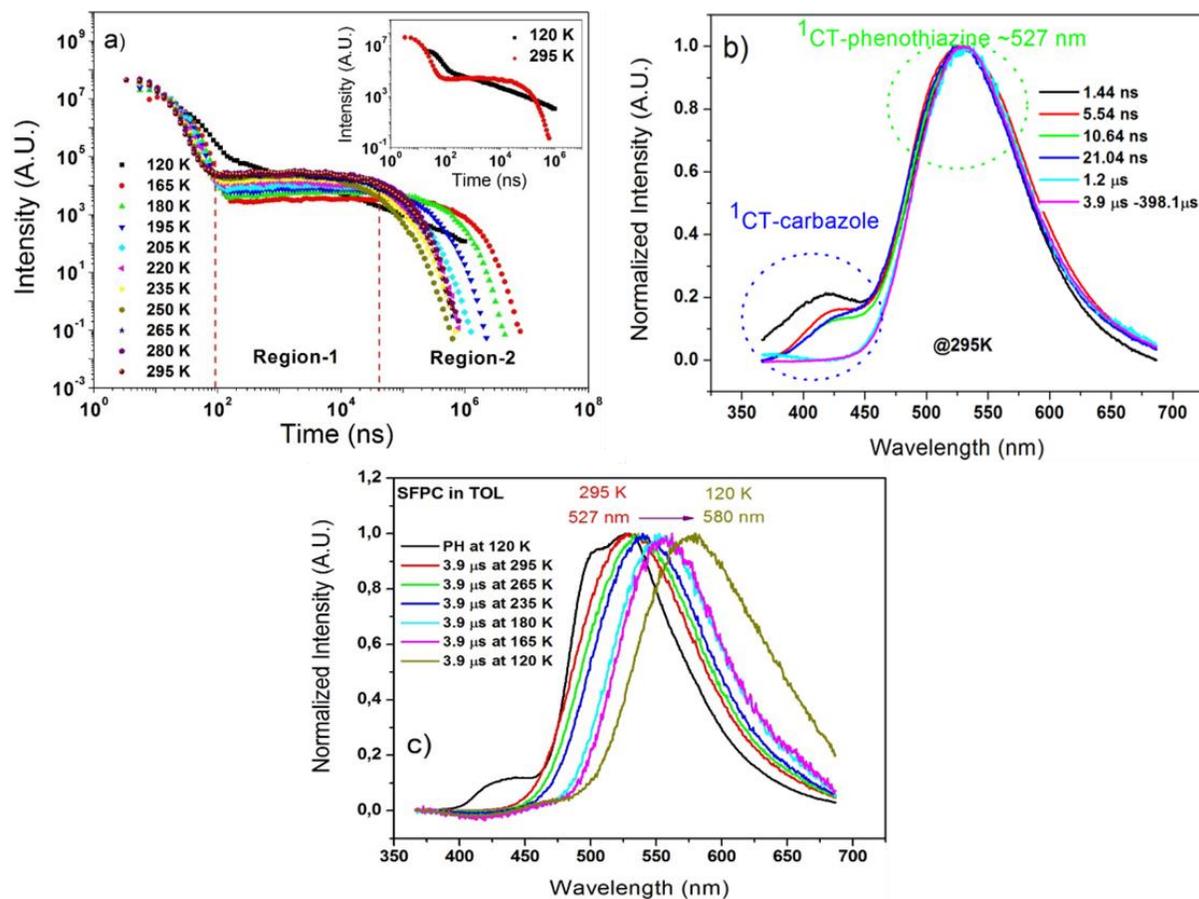
Figure 2. a) Time resolved emission decay of SFPC in TOL solution at variety of temperatures. The vertical dashed lines define the crossing points at 74 ns and 44.6 µs. The inserted plot is for comparison of the decays at 295 K and 120 K. **b)** Normalized time evolution spectra of SFPC in TOL solution at 295 K. **c)** The temperature dependent shift is represented for SF-[1]CT-phenothiazine emission , as the temperature is decreased from 295 K to 120 K, the emission shifts from 527 nm to 580 nm, respectively. Also, the [1]CT emission shift is compared with the PH emission to show how the energy gap between [3]LE and SF-P [1]CT state increases at low temperatures.

The excitation intensity dependence of the DF in "Region 1" (Fig. 2a) was determined as a function of the laser excitation dose, and a linear gradient of ~1 was found (see Fig. S7 in SI), which confirms that a monomolecular (thermally activated) DF mechanism is operative in this

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region. From the decay curve in Fig. 2a, "Region 2" can be defines as starting around 44.6 μs where the triplet harvesting is significant between the temperatures of 295 K- 220 K. However, when the temperature decreases below 200 K, the DF start time for "Region 2" shifts to longer times. This results in an inverse temperature dependency on the decay curve, where the intensity of emission slightly increases as the temperature decreases below 200 K. Similar behaviour was observed with a previous symmetrical D-A-D system (D= phenoxazine; A= 9,9-dimethylthioxanthene-*S-S*-dioxide:DPO-TXO2)[23] and was explained by two factors: i) due to enhanced radiative competition between an active TADF mechanism (^{3}LE→^{1}CT) and phosphorescence (^{3}LE→S$_0$); ii) increased dielectric constant of the solvent at low temperatures; this widens the ^{1}CT ^{3}LE gap which slows down the rate of ISC as well as rISC. [20] Consequently, ^{1}CT states convert to triplet states more slowly and those triplets return *via* rISC also more slowly such that the onset of DF then appears to slow down.
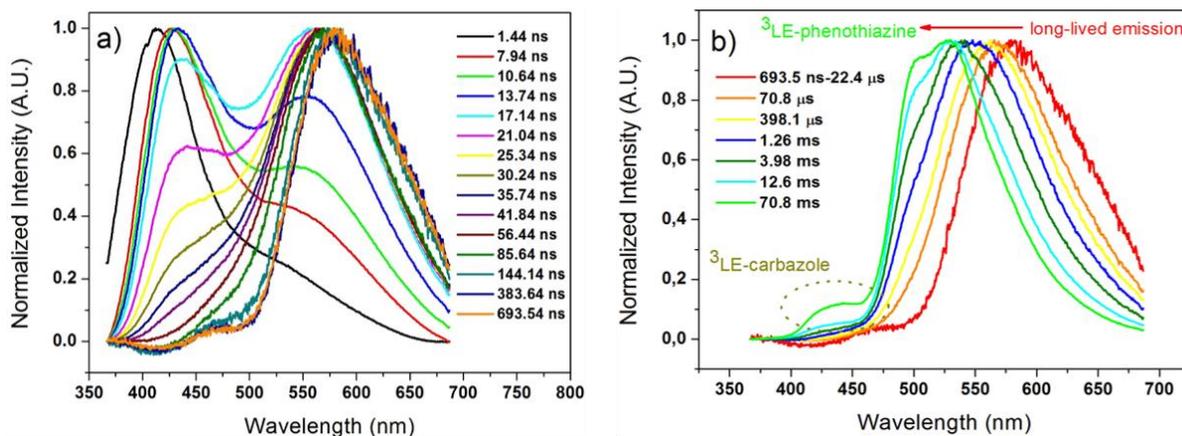

Figure 3. Normalized time evolution emission spectra of SFPC within the time regions of **a)** 1.44 ns to 693.54 ns in TOL solution at 120 K **b)** 693.54 ns to 70.8 ms in TOL solution at 120 K.

At 120 K, the analysis of the normalized SFPC spectra seems quite complex (Fig. 3 a). As the polarity of the toluene is much higher at 120 K than at 295 K, the [1]CT state of the SF-C A-D pair is stabilized and much stronger emission is overserved from this state at 120K, but again it decays far more rapidly than that of the SF-P A-D pair. The SF-C [1]CT state also clearly relaxes over the first 5-6 ns, indicative of increasing torsion angle between D-A units evolving with time (again stabilizing the CT state). The non-normalized time resolved emission spectra are shown in Fig. S8 in SI. No isoemissive point is seen in the decay indicating that the SF-C [1]CT excited states are not quenched by energy transfer to form the SF-P [1]CT excited state, i.e. both excited states are independent of each other.

At increasing time delay, the strong SF-C [1]CT emission (*ca*. 426 nm) decays and only SF-P [1]CT emission remains at longer wavelengths (*ca.* 569 nm). At late delay times, an isoemissive point is observed (Fig. 3 a) at *ca.* 569 nm with the emission red shifting (between 693.5 ns to 22.4 μs) with the SF-P [1]CT emission peaks ending up at *ca.* 580 nm. It should be noted that this SF-P [1]CT state is independent of solution concentration and temperature, and always exists at late delayed times, therefore, it cannot be explained with an "aggregation-induced" phenomena.[26,27] Instead, it reflects the fast decay of the (blue) SF-C [1]CT emission leaving only the (long-lived green) SF-P [1]CT emission. This isoemissive point appears in the area normalised spectra, indicating that these two species are not linked, i.e. one does not feed the other, they are independent emitters, confirming what is seen in the non-normalized data (see Fig. S8 in SI). After 22.4 μs delay time, the Gaussian shaped green emission shows a progressively blue shift with time and the emission reverts to phosphorescence (PH) from a locally excited triplet state, as in Fig. 3 b. At very late delay times (i.e. 70.8 ms), the PH of SFPC is completely stabilized and reflects the simultaneous contributions from [3]LE-phenothiazine (strong green-emission) and

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[3]LE-carbazole (weak blue-emission) states; therefore, a dual-PH spectrum appears (see Fig. S2 in SI). In the same figure, the PH spectra of the symmetric molecules, SF2C and SF2P, are compared with asymmetric SFPC molecule, where a perfect spectral match is observed between SF2P and the "green" part of the SFPC spectrum, corroborating that a significant portion of triplet emission observed in SFPC clearly comes from a locally excited triplet state of the donor phenothiazine unit. In addition, the energy of the [3]LE-phenothiazine state is also determined from the first vibronic of the PH spectra as 2.48 ± 0.01 eV. The small bump on the blue shoulder of the PH spectrum of SFPC matches with the PH spectrum of SF2C, confirming the involvement of [3]LE- carbazole state in the PH emission of SFPC.

The excited state dynamics of SFPC was also investigated in 2-MeTHF solution (Fig. 4), where the emission retains the same CT character as observed in toluene. However, due to the higher polarity of 2-MeTHF ($\varepsilon = 6.24$ at 298 K rising to 13.4 at 143K, [32] ground state dipole moment $\mu=1.38$D), the SF-P [1]CT emission slightly shifts to lower energies, whereas, more importantly, the PH spectrum shifts to higher energies (Fig. S9 in SI). In particular, the blue shift in energy is significant in the [3]LE-phenothiazine state, indicating that this state presumably has strong $^3(n\pi^*)$ character.[33] However, when comparing the PH features of SFPC in toluene and 2-MeTHF, no significant change is observed in the energy of the [3]LE-carbazole state, indicating strong $^3(\pi\pi^*)$ character. The emission of [3]LE-carbazole is strong and makes a significant contribution to the overall PH emission of SFPC with long lifetime (~ 255 ms), which is shorter than the PH lifetime of SF2C in 2-MeTHF, ~370 ms.

From the time evolution of the spectra of SFPC, a weak tail of the [1]LE-carbazole emission is detected at 1.44 ns delay time (at 295 K) (Fig. 4a). However, it becomes stronger as the temperature decreases, peaking *ca.* 433 nm at 225 K (Fig. 4b), indicating a slower electron

transfer step and/or stabilization of the SF-C ^{1}CT state, the latter in line with the increasing polarity of the solvent as the temperature reduces.[34] After a few nanoseconds (i.e. 5.54 ns) at 295 K, the detected dual-emission spectrum mainly reflects the emission from SF-P ^{1}CT and SF-C ^{1}CT states. Again, no DF originates from the SF-C ^{1}CT state. Instead, the SF-P ^{1}CT state is the dominant TADF emitter, with all DF peaking at *ca.* 560 nm at 295 K and shifting progressively to longer wavelengths as the temperature is decreased, peaking at *ca.* 576 nm at 225 K and *ca.* 614 nm at 150 K (Fig. 4c and 4d). Again this is due to the changing polarity of the solvent, which causes an increase in energy gap between the ^{3}LE and SF-P ^{1}CT states and concomitantly the TADF is less efficient, which gives rise to the weak and reduced emission spectra at 150 K (Fig. 4d).
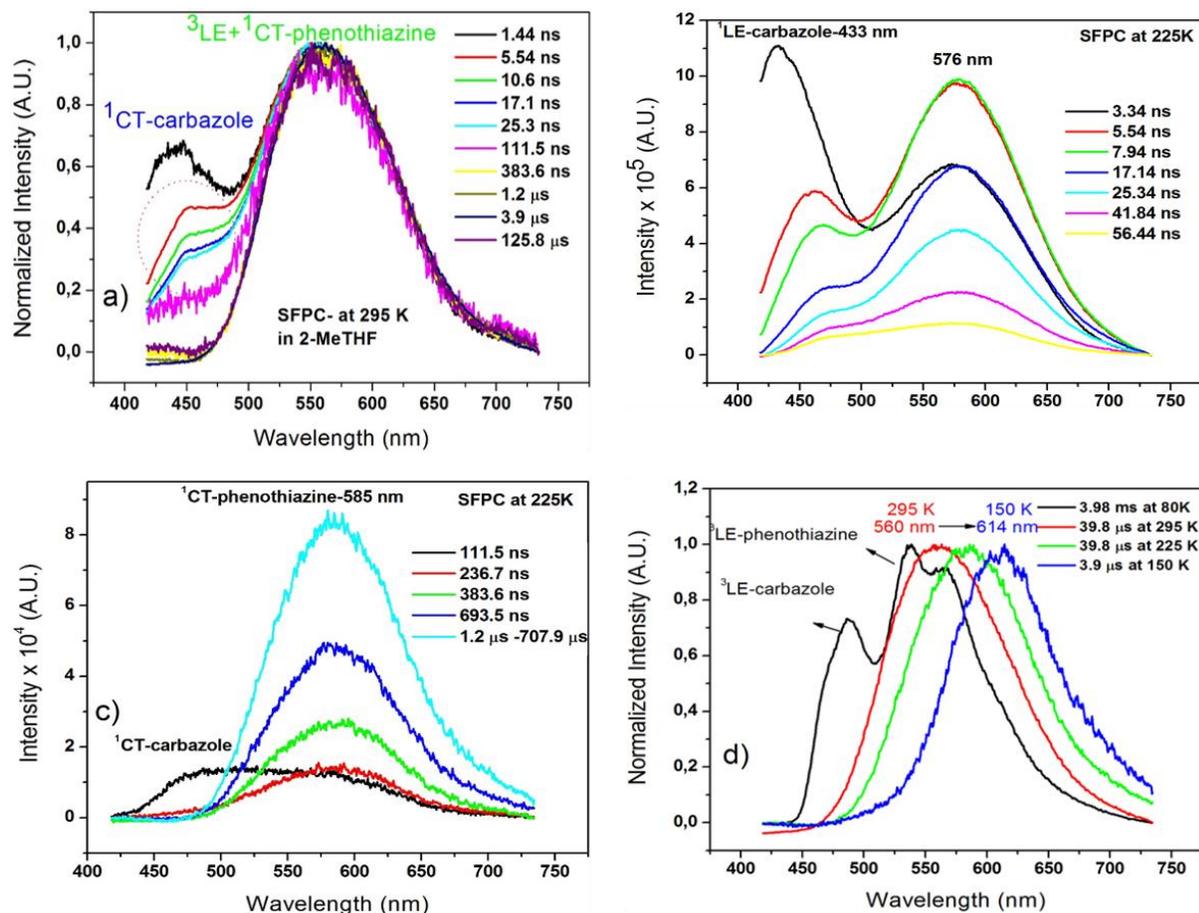
Figure 4. Time evolution spectra of SFPC in 2-MeTHF, where the delay time is between **a)** 1.44 ns and 125.8 μs at 295 K **b)** 3.34 ns and 56.44 ns at 225 K **c)** 111.5 ns and 707.9 μs at 225 K. **d)** The change in onset and peak position of SF-P ^{1}CT emission spectra at 295 K, 225 K and 150 K, and PH spectrum at 80 K is plotted for comparison.

Reducing the temperature makes the ^{1}LE and SF-C ^{1}CT emissions much stronger, where the localized excitonic ^{1}LE-carbazole state emits at *ca.* 433 nm at 225 K and 150 K (Fig. 5a), electron transfer is slowed even further, and a clear build-in of the SF-C ^{1}CT state emission over 30 ns is seen. The SF-C ^{1}CT state does not show energy transfer to the SF-P ^{1}CT state, as at 17 ns we can observe ^{1}LE-carbazole emission with a small shoulder from the SF-C ^{1}CT state and SF-P ^{1}CT emission simultaneously. Indeed, between 85.64 ns and 209.44 ns delay times, the emission from the SF-C ^{1}CT state totally dominates the spectra and peaks at *ca.* 503 nm (Fig. 5b). At this temperature (150 K) quenching of the SF-C ^{1}CT state has been stopped and the true lifetime of the SF-C ^{1}CT state is seen. This indicates that either a vibrational mode is turned off such that internal conversion is stopped, or a back rotation of the SF-C part is slowed down sufficiently that the SF-C ^{1}CT state is stabilized and lives long enough to emit efficiently. After 383.6 ns delay time, the SF-C ^{1}CT state has decayed, and the emission from SF-P ^{1}CT state dominates the whole system until the delay time of 22.4 μs (Fig. 5b). Therefore, it can be seen that active molecular torsional motions (at 150 K) are still able vibronically couple SF-P ^{1}CT and ^{3}LE-phenothiazine states to harvest the triplet state resulting in long-lived emission at about ~610 nm (Fig. 5b). Again these new findings are incompatible with the previously considered "aggregation-induced" TADF features,[26] and reveal the key role of the relative orientation within the D-A-D' structure and the dynamic re-orientation of the D-A and A-D' moieties of each emissive states.
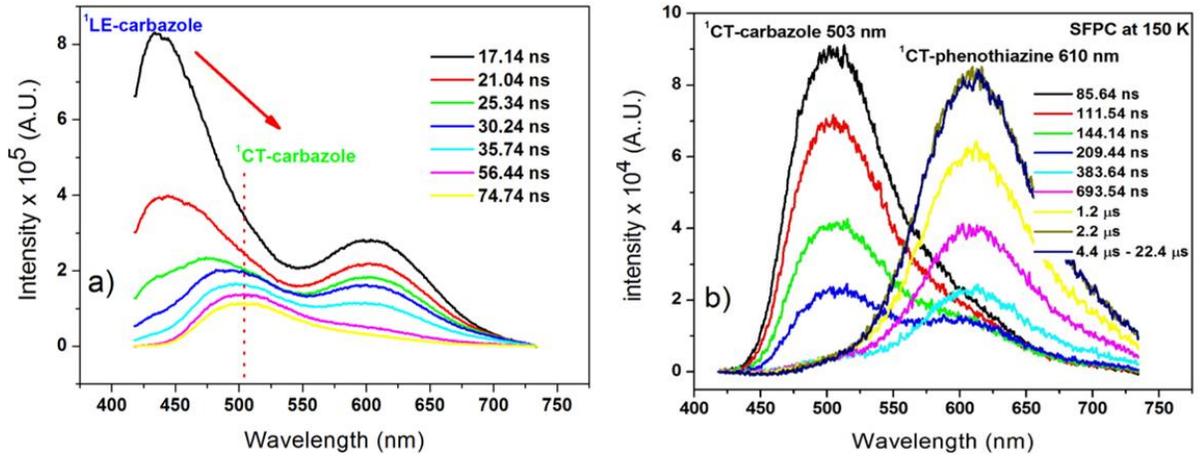
Figure 5. Time evolution spectra of SFPC in 2-MeTHF at 150 K, where the delay time is between **a)** 17.14 ns and 74.74 ns **b)** 85.64 ns and 22.4 μs.
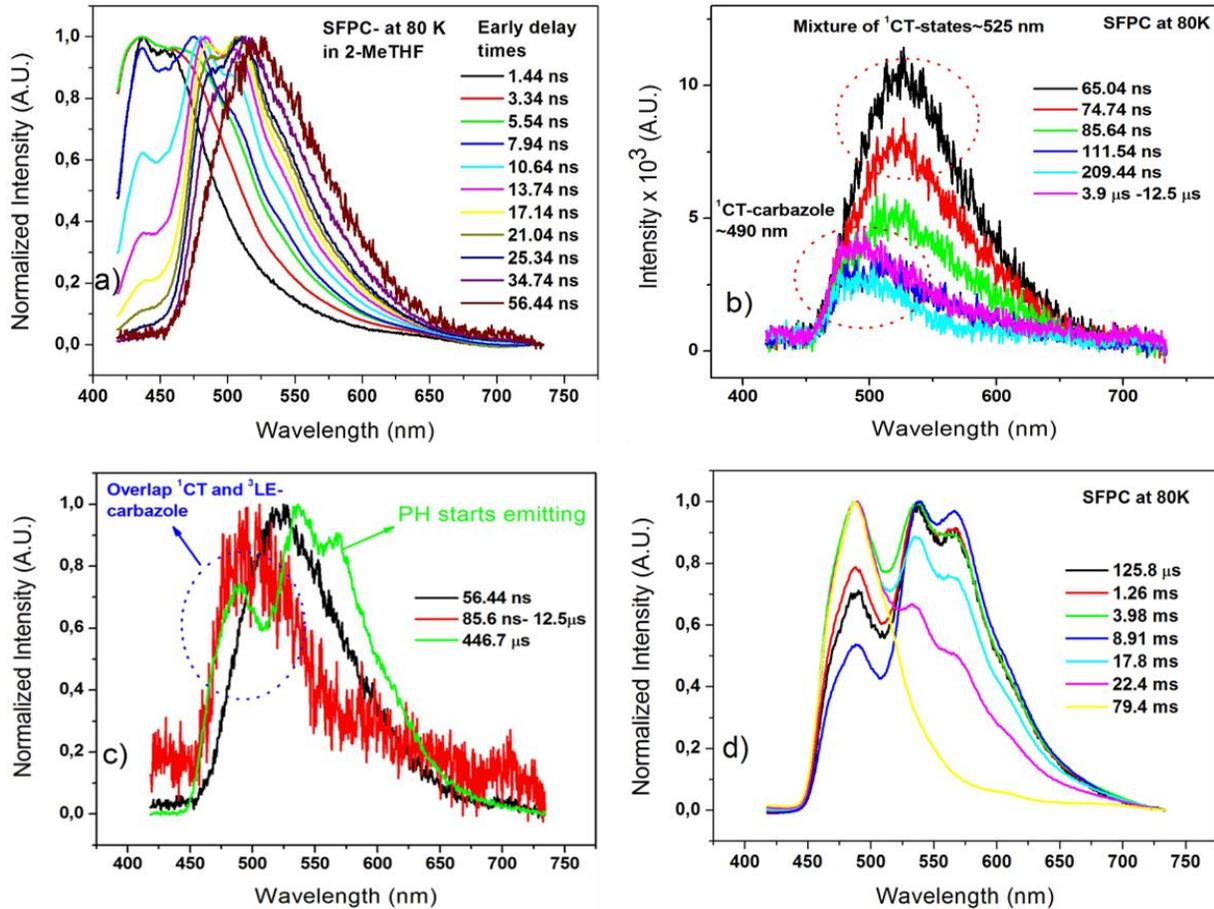
Figure 6. a) Time evolution spectra of SFPC in 2-MeTHF solution at 80 K, where the delayed time is between **a)** 1.44 ns and 56.44 ns **b)** 65.04 ns and 12.5 μs. **c)** The emission spectra are compared different time regimes to determine the origin of the emissions. **d)** The PH spectra of SFPC represent contributions of both [3]LE-phenothiazine and carbazole states, where the latter have relatively long lifetime.

At 80 K, where the 2-MeTHF solvent is frozen, both [1]LE-carbazole and [1]LE-phenothiazine emission of SFPC can be detected strongly at early delay times (i.e. between 1.44 ns and 21.04 ns, Fig. 6a). The fact that they are observed as simultaneously emitting species indicates very slow electron transfer and little energy transfer between the two donor states, which is surprising observation and we assume is a consequence of the relative orientation of the two donors. After 21.04 ns delayed times, the emission from the [1]LE-carbazole species has totally decayed and dual [1]LE-phenothiazine and SF-P [1]CT remains; the [1]LE-phenothiazine emission decays by 56.44 ns. The remaining SF-P [1]CT emission peaks at *ca.* 525 nm, showing very little solvent polarity stabilization, indicative of the frozen solution. The SF-P [1]CT state decays rapidly because no DF occurs at 80 K and so only the prompt SF-P [1]CT is observed (having a relatively short lifetime). By 4 μs, the SF-C [1]CT emission is very weak (Fig. 6b), peaking *ca.* 490 nm. This now shows that the SF-P [1]CT state lifetime is both stabilized by solvent polarity and effectively lengthened by DF, as at 80 K no rISC can occur and so there is no DF contribution. However, the SF-C [1]CT states are stabilized by a retardation of the back torsional motion of D-A, the frozen solution locks-in a twisted SF-C conformation, and consequently very long-lived SF-C [1]CT emission is observed, even into the 4-12 μs times. After 446.7 μs, emission from both [3]LE states (carbazole and phenothiazine) is observed (Fig. 6c). Now it can be seen that the carbazole [3]LE has a much

longer lifetime than the phenothiazine ^{3}LE state (Fig. 6d). Again, at 80 K, the quenching of the ^{3}LE states is much reduced, especially the carbazole ^{3}LE state.

4. Conclusion

We have particularly focused on the excited state photophysical properties of an asymmetric TADF emitter, SFPC, which was previously claimed [22] as an "aggregation-induced" TADF emitter due to the molecule showing excellent packing and highly ordered alignment between D-A-D' moieties. Indeed, in the parent (symmetric) D-A-D molecules the relative orientations of D-A units are near planar in SF2C and near-orthogonal in SF2P, which makes the CT state in SF2C rather weak with little solvent stabilization and consequently almost pure ^{1}LE emission appears in non-polar media. In contrast, in SF2P, the CT state is much stronger, even in non-polar media and undergoes far greater solvent stabilization in polar media. We also observe the strong effects in emission bands due to the temperature dependence of solvent polarity. In addition, the geometry of the asymmetric SFPC molecule is near planar-orthogonal, where the green- emitting SF-P ^{1}CT state is found to be independent of solution concentration and temperature, and always exists at late delayed times. Furthermore, one of the most important findings of the work is that the SF-C ^{1}CT excited state is not quenched by energy transfer to form the lower energy SF-P ^{1}CT excited state; both excited states are independent of each other. This also seems to be true for the excited donors as well, as there is little evidence of energy transfer from the excited carbazole donor to the phenothiazine donor, a result which confirms the orthogonality between the donor moieties as a result of the planar-orthogonal conformation of the asymmetric molecule. This is an important and very unusual observation, and shows that dual CT emission from an asymmetric D-A-D' molecule can be used in an OLED to give very broad emission,[22] which is controlled by the molecular conformation of this D-A-D' system. The strong solvent effect on CT

emission is shown to be the cause of what previously was attributed to an "aggregation-induced" emission phenomena. We clearly observe a strong red shift and decrease in emission intensity as the polarity increases until the D-A-D' molecule precipitates. At this point the solid is a far less polar environment then the solvent and the spectra blue shift with the concomitant increase in emission intensity. This is not AIE.

Associated Content

Supporting information. Figures S1 to S9 are available free of charge *via* the internet at http://pubs.acs.org

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Author Contributions

The manuscript was written through contributions of all authors. Z. C., S. X and C. C. synthesized the materials and made chemical and x-ray analysis. M. A. made all of the photophysical measurements. A. P. M. designed the photophysical studies, analyzed the data and developed the physical interpretation All authors have given approval to the final version of the manuscript. M.A., M.R.B. and A.P.M. wrote the manuscript.

References

1. Burroughes, J. H.; Bradley, D.D.C.; Brown, A.R.; Marks, R.N.; Mackay, K.; Friend, R.H.; Burn, P.L.; Holmes, A.B., Light-emitting diodes based on conjugated polymers. *Nature* **1990**, *347***,** 539–541.

2. Tang, C. W.; VanSlyke, S. A., Organic Electroluminescent Diodes. *Appl. Phys. Lett.* **1987,** 51**,** 913–915.

3. Liang, J.; Li, L.; Niu, X.; Yu, Z.; Pei, Q., Elastomeric polymer light-emitting devices and displays. *Nat. Photonics* **2013**,**7,** 817–824.

4. Atkins, P. W. *Molecular quantum mechanics*. Oxford University Press **1983**.

5. Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R., Nearly 100% internal phosphorescence efficiency in an organic light-emitting device. *J. Appl. Phys.* **2001**, 90**,** 5048–5051.

6. Meerheim, R.; Walzer, K.; Pfeiffer, M.; Leo, K., Ultrastable and efficient red organic light emitting diodes with doped transport layers. *Appl. Phys. Lett.* **2006**, 89**,** 061111.

7. Liao, L. S.; Klubek, K. P.; Tang, C. W., High-efficiency tandem organic light-emitting diodes. *Appl. Phys. Lett.* **2004**, 84, 167–169.

8. Duan, L.; Qiao, J.; Sun, Y.; Qiu, Y., Strategies to Design Bipolar Small Molecules for OLEDs: Donor-Acceptor Structure and Non-Donor-Acceptor Structure. *Adv. Mater.* **2011**, 23, 1137–1144.

9. Lee, S. Y.; Yasuda, T.; Nomura, H.; Adachi, C., High-efficiency organic light-emitting diodes utilizing thermally activated delayed fluorescence from triazine-based donor-acceptor hybrid molecules. *Appl. Phys. Lett.* **2012**, 101, 093306.

10. Jenekhe, S. A.; Lu, L. D.; Alam, M. M., New conjugated polymers with donor-acceptor architectures: Synthesis and photophysics of carbazole-quinoline and phenothiazine-quinoline copolymers and oligomers exhibiting large intramolecular charge transfer. *Macromolecules* **2001**, 34, 7315–7324.

11. Jankus, V.; Chiang, C.-J.; Dias, F.; Monkman, A. P., Deep Blue Exciplex Organic Light-Emitting Diodes with Enhanced Efficiency; P-type or E-type Triplet Conversion to Singlet Excitons? *Adv. Mater.* **2013,** 25, 1455–1459.

12. Tanaka, H.; Shizu, K.; Nakanotani, H.; Adachi, C., Twisted Intramolecular Charge Transfer State for Long-Wavelength Thermally Activated Delayed Fluorescence. *Chem. Mater.* **2013**, 25, 3766–3771.

13. Etherington M.K, Higginbotham H.F, Gibson J.; Penfold T.J. and Monkman A.P. Revealing the spin-vibronic coupling mechanism of thermally activated delayed fluorescence. *Nat. Commun.* **2016**, 7, 13680.

14. Etherington, M. K.; Franchello, F.; Gibson, J.; Northey, T.; Santos, J.; Ward, S.J.; Higginbotham, H.F.; Data, P.; Kurowska, A.; Dos Santos, P.L.; et al., Regio- and conformational isomerization critical to design of efficient thermally-activated delayed fluorescence emitters. *Nat. Commun.* **2017**, 8**,** 14987.

15. Daub, J.; Engl, R.; Kurzawa, J.; Miller, S.E.; Schneider, S.; Stockmann, A., Wasielewski Competition between conformational relaxation and intramolecular electron transfer within phenothiazine-pyrene dyads. *J. Phys. Chem. A* **2001**, 105**,** 5655–5665.

16. Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W., Structural changes accompanying intramolecular electron transfer: Focus on twisted intramolecular charge-transfer states and structures. *Chem. Rev.* **2003**, 103**,** 3899–4031.

17. Aydemir, M.; Haykir, G.; Turksoy, F.; Gumus, S.; Dias, F.B.; Monkman, A.P., Synthesis and investigation of intra-molecular charge transfer state properties of novel donor-acceptor-donor pyridine derivatives: the effects of temperature and environment on molecular configurations and the origin of delayed fluorescence. *Phys. Chem. Chem. Phys.* **2015**, 17**,** 25572–25582.

18. Dias, F. B.; Bourdakos, K.N.; Jankus, V.; Moss, K.C.; Kamtekar, K.T.; Bhalla, V.; Santos. J.; Bryce, M.R.; Monkman, A.P., Triplet Harvesting with 100% Efficiency by Way of Thermally Activated Delayed Fluorescence in Charge Transfer OLED Emitters. *Adv. Mater.* **2013**, 25**,** 3707–3714.

19. Penfold, T. J., On Predicting the Excited-State Properties of Thermally Activated Delayed Fluorescence Emitters. *J. Phys. Chem. C* **2015**, 119**,** 13535–13544.

20. Gibson, J.; Monkman, A. P.; Penfold, T. J., The Importance of Vibronic Coupling for Efficient Reverse Intersystem Crossing in Thermally Activated Delayed Fluorescence Molecules. *ChemPhysChem* **2016**, 17**,** 2956–2961.

21. Baleizao, C.; Berberan-Santos, M. N., Thermally activated delayed fluorescence as a cycling process between excited singlet and triplet states: Application to the fullerenes. *J. Chem. Phys.* **2007**, 126**,** 204510.

22. Dias, F. B.; Santos, J.; Graves, D.R.; Data, P.; Nobuyasu, R.S.; Fox, M.A.; Batsanov, A.S.; Palmeira, T.; Berberan-Santos, M.N.; Bryce, M.R.; et al., The Role of Local Triplet Excited

States and D-A Relative Orientation in Thermally Activated Delayed Fluorescence: Photophysics and Devices. *Adv. Sci.* **2016**, 1600080.

23. Santos, P.; Ward, J.S.; Data, P.; Batsanov, A.S.; Bryce, M.R.; Dias, F.B.; Monkman, A.P., Engineering the singlet-triplet energy splitting in a TADF molecule. *J. Mater. Chem. C* **2016,** 4, 3815–3824.

24. Jankus, V.; Aydemir, M.; Dias, F. B.; Monkman, A. P., Generating Light from Upper Excited Triplet States: A Contribution to the Indirect Singlet Yield of a Polymer OLED, Helping to Exceed the 25% Singlet Exciton Limit. *Adv. Sci.* **2016**, 3**,** 1500221.

25 Lim, B.; Okajima, S.; Chandra, A.; Lim, E., Radiationless Transitions in Electron Donor-Acceptor Complexes - Selection-Rules for S1-T1 Intersystem Crossing and Efficiency of S1-S0 Internal-Conversion. *Chem. Phys. Lett.* **1981,** 79**,** 22–27.

26 Xu, S.; Liu, T.; Mu, Y.; Wang, Y.F.; Chi, Z.; Lo, C.C.; Liu, S.; Zhang, Y.; Lien, A.; Xu, J., An Organic Molecule with Asymmetric Structure Exhibiting Aggregation-Induced Emission, Delayed Fluorescence, and Mechanoluminescence. *d Angew. Chem. Int. Ed.* **2015,** 54**,** 874–878.

27. Xie Z.; Chen, C.; Xu., S.; Zhang, Y.; Liu, S.; Xu, J.; Chi, Z., White-Light Emission Strategy of a Single Organic Compound with Aggregation-Induced Emission and Delayed Fluorescence Properties. *Angew. Chem. - Int. Ed.* **2015**, 54, 7181–7184.

28. Stockmann, A.; Kurzawa, J.; Fritz, N.; Acar, N.; Schneider, S.; Daub, J.; Engl, R.; Clark, T., Conformational control of photoinduced charge separation within phenothiazine-pyrene dyads. *J. Phys. Chem. A* **2002**, 106**,** 7958–7970.

29. Jankus, V.; Monkman, A. P., Is Poly(vinylcarbazole) a Good Host for Blue Phosphorescent Dopants in PLEDs? Dimer Formation and Their Effects on the Triplet Energy Level of Poly(N-vinylcarbazole) and Poly(N-Ethyl-2-Vinylcarbazole). *Adv. Funct. Mater.* **2011**, 21**,** 3350–3356.

30. Rothe, C.; Monkman, A. P., Triplet exciton migration in a conjugated polyfluorene. *Phys. Rev. B* **2003**, 68**,** 075208.

31. Bublitz, G. U.; Boxer, S. G., Effective Polarity of Frozen Solvent Glasses in the Vicinity of Dipolar Solutes. *J. Am. Chem. Soc.* **1998**, 120**,** 3988–3992.

32. Zoon, P.D.; Brouwer, A.M., A push-pull aromatic chromophore with a touch of merocyanine. *Photochem. Photobiol. Sci. Off. J. Eur. Photochem. Assoc. Eur. Soc. Photobiol.* **2009**, 8, 345–53.

33. Chaudhuri, D.; Sigmund, E.; Meyer, A.; Rock, L.; Klemm, P.; Lautenschlager, S.; Schmind, A.; Yost, S.R.; Voorhis, T.V.; Bange, S.; et al., Metal-Free OLED Triplet Emitters by Side-Stepping Kasha's Rule. *Angew. Chem. Int. Ed.* **2013**, 52, 13449–13452.

34. Damrauer, N. H.; McCusker, J. K., Variable-temperature emission studies of solvation dynamics: Evidence for coupling of solvation to chromophore structural dynamics in the evolution of charge-transfer excited states. *Inorg. Chem.* **1999**, 38**,** 4268–4277.

Supporting Information

The Photophysics of an Asymmetric Donor-Acceptor-Donor' TADF Molecule and Reinterpretation of Aggregation Induced TADF Emission in these materials.

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SUPPORTING INFORMATION (SI):
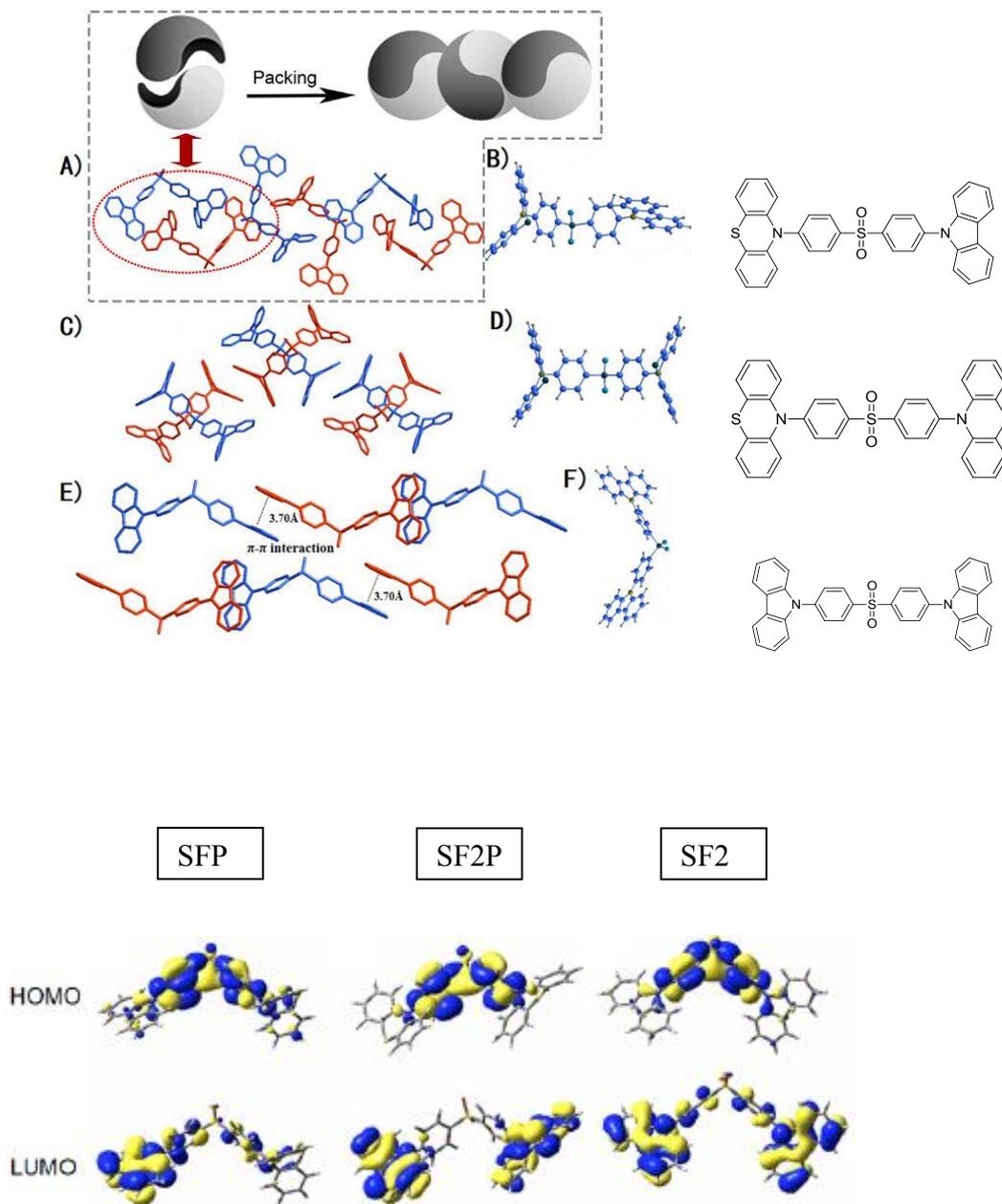
Figure S1. The diagrams represent the packing, interaction and structures of SFPC (A and B), SF2P (C and D) and SF2C (E and F) in their X-ray crystal structures The geometry of D A units in the asymmetric SFPC appears axial-equatorial, SF2P is equatorial-equatorial (terminology after Stockmann, A. *et al.* Conformational control of photoinduced charge separation within

phenothiazine-pyrene dyads. *J. Phys. Chem. A* **106,** 7958–7970 (2002)) and SF2C is near planar. Electron density distributions in HOMO-LUMO energy levels of molecules. The picture is adapted from Ref.[21]
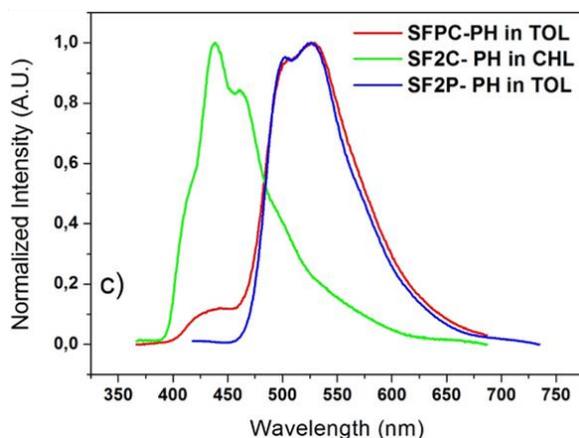
Figure S2. The emission spectra of PH for SFPC (in TOL), SF2C (in CHL) and SF2P (in TOL).
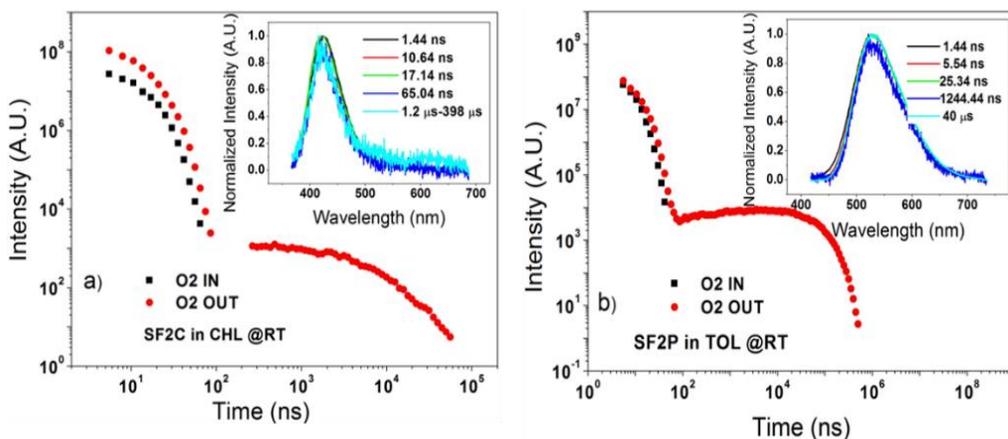
Figure S3. Time-resolved decay of **a)** SF2C in aerated (black dots) and non-aerated (red dots) CHL solution at RT and inserted plot shows the time evolution of emission spectra between 1.44 ns to 398 μs **b)** SF2P in aerated (black dots) and non-aerated (red dots) TOL solution at RT and inserted plot shows the time evolution of emission spectra between 1.44 ns to 40 μs.
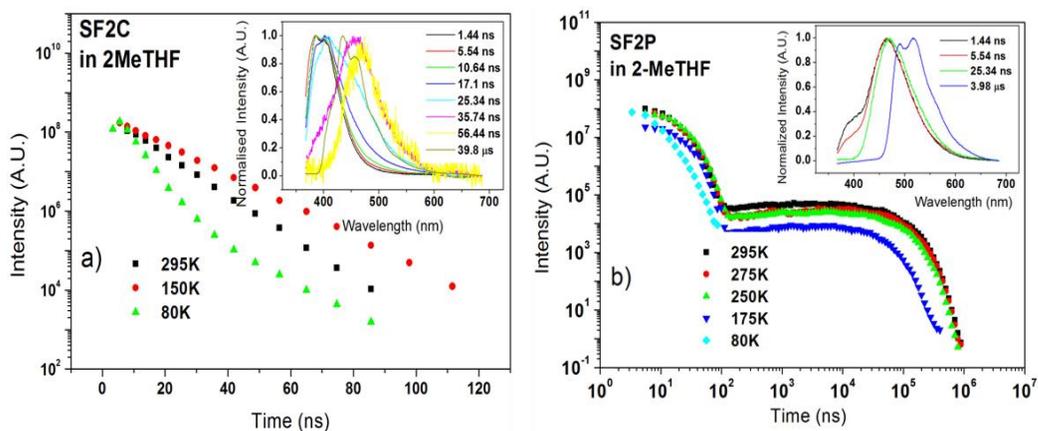
Figure S4. Time resolved fluorescence decay of SF2C **(a)** and SF2P **(b)** molecules in 2-MeTHF solution at a variety of temperatures. The inserted graphs represent the time resolved normalized emission spectra at 80 K.
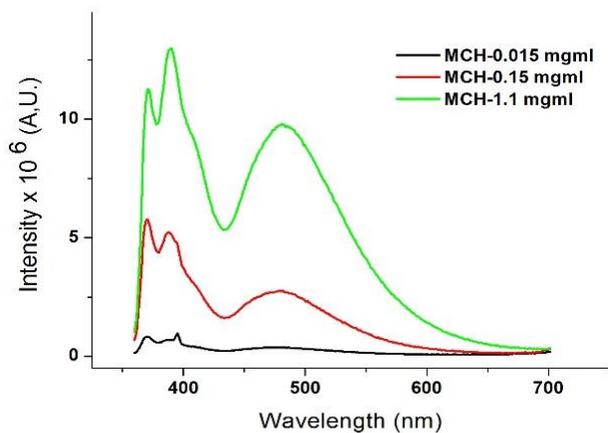

Figure S5. The change in steady-state emission spectra of SFPC in three different MCH concentrations, 0.015 mg/ml, 0.15 mg/ml and 1.1 mg/ml
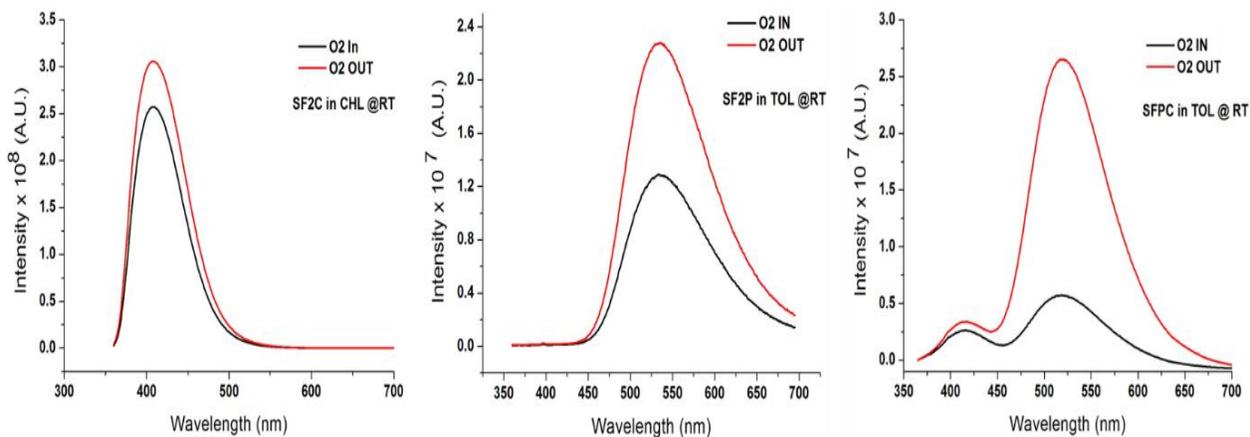
Figure S6. The change in intensity of emission in non-aerated solutions at RT from left to right, SF2C (in CHL), SF2P (in TOL) and SFPC (in TOL)
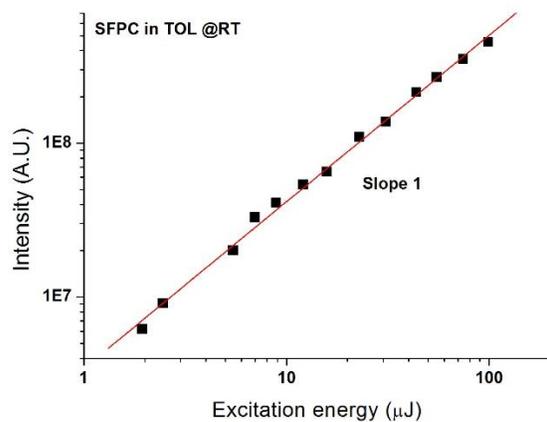

Figure S7. Laser fluency dependence of SFPC-DF in degassed TOL solution at RT, where the delay and integration time are chosen as 1.2 µs and 20 µs, respectively.
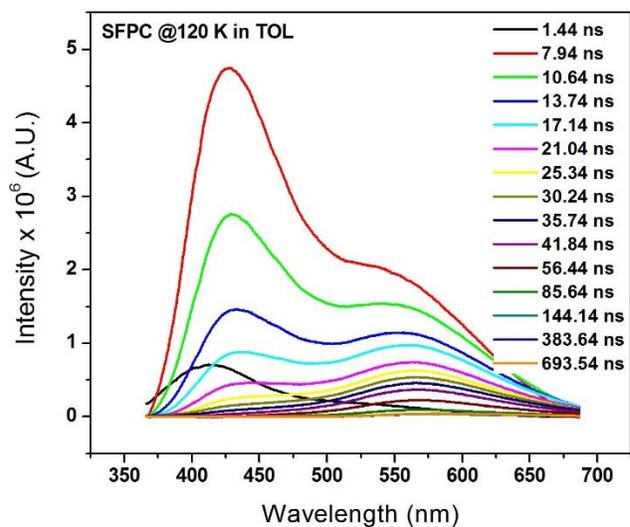
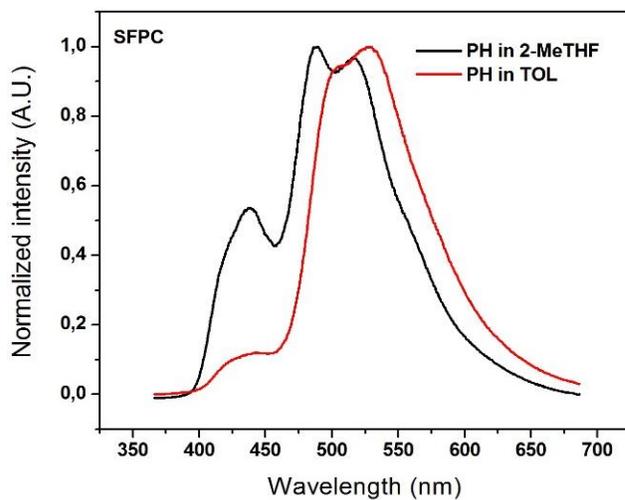**Figure S8.** The Non-normalized time resolved emission spectra of SFPC in TOL at 120 K.

Figure S9. The PH spectra of SFPC in toluene and 2-MeTHF solutions.