

Intramolecular Interchromophore Singlet-Singlet and Triplet- Singlet Energy Transfer in a Metal-Free Donor-Acceptor Emitter

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Abstract

In this work we demonstrate the occurrence of singlet to singlet, and triplet to singlet, intramolecular energy transfer occurring between two thiophene-comprising donors (D) and a central perylene bisimide acceptor (A) covalently linked to each other through a linker structure that separates the donor and acceptor moieties in a D-A-D structure. The designed metal-free organic tandem luminophore is herein designated as **ARC-1467**. Energy transfer from the excited triplet state of the thiophene donor to the singlet state of the perylene bisimide acceptor is observed in solution and in solid films of **ARC-1467** dispersed in polystyrene. When the perylene bisimide acceptor is directly excited, the fluorescence decays with 4.9 ns lifetime. However, upon excitation of the donor unit in the near-UV region, delayed fluorescence of perylene bisimide with 5.7 μ s lifetime is distinctly observed demonstrating the occurrence of energy transfer from the triplet state of the D unit to the perylene bisimide acceptor.

Introduction

Harvesting energy of excited triple states in organic compounds is of key importance in different areas of technology, including the design of luminophores with persistent

luminescence,[1,2] which can be applied in anti-counterfeiting inks,[3] signage coatings,[4] bioimaging and oxygen sensing,[5] and the development of emitters for application in organic light emitting diodes (OLEDs) and light emitting electrochemical cells (LECs).[6] In the former, the aim is to design materials that simultaneously show extended lifetimes and luminescence yields. This requires promoting fast intersystem crossing (ISC) and reducing quenching of the triplet population.[7] Biluminescent emitters showing emissions from both singlet and triplet states and emitters with persistent luminescence are mainly based on molecular structures with $n-\pi^*$ transitions that aim to enhance intersystem crossing (ISC), and often use crystalline arrangements or hydrogen bonding structures where intermolecular interactions suppress internal conversion to maximize phosphorescence.[8,9] In OLEDs and LECs, the aim is to harvest, and upconvert, triplet states into emissive singlet states. As charge recombination creates three times more dark triplets than emissive singlet states, the conversion of non-emissive triplets into emissive singlet states is crucial to maximize device efficiency. If only pure fluorescent emitters are used, the internal efficiency of OLEDs and LECs is limited to 25%. However, with triplet harvesting 100% efficiency is attainable.[10] It is also desirable that harvesting of the triplet states occurs rapidly, to minimize non-linear quenching processes that contribute to the device efficiency roll-off due to interactions of long-lived excited states with charges.[11]

Different mechanisms have been proposed to convert dark triplet states into emissive species. The most prominent examples are organic metal complexes,[10] and thermally activated delayed fluorescence (TADF) emitters.[6,12] Organic heavy-metal complexes explore the enhanced spin-orbit coupling interactions created by the metal centre to accelerate the decay rate of the triplet state. These compounds show very

fast ISC rates, rendering triplet yields close to 100%, and bright phosphorescence emission across the visible spectrum. Unfortunately, no stable blue emitter based on heavy-metal complexes has been found yet. Moreover, these complexes may create environmental and cost challenges, if they are to be used for the manufacturing of large-scale products, as in the lighting and display industries. On the other hand, TADF emitters were introduced recently as a viable alternative to heavy-metal complexes.[6] The design of TADF materials is mostly based on excited states with charge transfer character (CT) created by the interaction between electron donor and electron acceptor units that are covalently linked to each other in quasi-orthogonal orientation. This alignment minimizes the overlap between the D/A frontier molecular orbitals, resulting in singlet and triplet states of similar energy, therefore, achieving extremely small singlet-triplet energy gaps. Non-emissive triplet states can thus be upconverted to the singlet manifold *via* thermally activated reverse intersystem crossing. TADF emitters appear to be more stable than heavy-metal complexes, especially in the blue region, and OLEDs with internal efficiency close to 100% have been demonstrated across the entire visible spectrum.[13] Additionally, the high sensitivity of the triplet harvesting mechanism to the surrounding medium, temperature, and oxygen gives TADF emitters great potential in environmental sensing and optical thermometry applications that remain largely unexplored.[14,15]

Despite the great potential and interest in triplet harvesting mechanisms, the possibility of harvesting triplet states through energy transfer to a singlet state in another molecule (or intramolecularly) has been almost ignored and often believed to be inefficient. However, based on theoretical considerations, Förster concluded in 1959 that in addition to singlet-singlet energy transfer, nonradiative long-range energy transfer should be possible from the excited triplet state of a sensitizer phosphor to the

singlet state of an acceptor under suitable conditions.[16] In 1963¹ Ermolaev and Sveshnikova were the first to report registration of the phenomenon of energy transfer of a triplet donor molecule to singlet acceptor molecule.[17] Energy transfer was established in rigid solutions (ethanol, 93 K) by the shortening of the decay time of phosphorescence of a donor (triphenylamine) in the presence of an acceptor molecule (chrysoidine, chlorophyll or pheophytin) whose absorption spectrum overlapped with the phosphorescence spectrum of the donor.[17]

In 2001, an approach was disclosed for construction of luminophores that display long emission wavelengths, long decay times, and high quantum yields.[18] The proposed tandem luminophore comprises a long-wavelength acceptor fluorophore (Texas Red dye) covalently linked by a short peptide chain to a pair of long-lifetime energy transfer donor (ruthenium metal-ligand complex). More recently, this mechanism was demonstrated in a molecular dyad formed by an Ir(III) complex donor covalently linked to perylene unit acceptor *via* bicyclo[2.2.2]octane bridge that was used to spatially separate the donor and acceptor moieties.[19] The rationale was based on selecting a donor unit capable of generating triplet states very rapidly and possessing phosphorescence emission spectrum overlapping the absorption of the acceptor unit to promote efficient triplet-to-singlet energy transfer. Additionally, the acceptor shows a small Stokes shift and large fluorescence quantum yield in order to minimize energy losses. Volyniuk et al. also reported blue OLEDs with 17% external efficiency (EQE), thus much higher than the 5% limit imposed on pure fluorescent emitters.[20] To explain the high EQE, the authors suggested that efficient intermolecular energy transfer was taking place from the triplet state of the host to the radiative singlet states

¹ A previous work from 1962, is cited in M. Inokuti and F. Hirayama, J. Chem. Phys. 43, 1978 (1965) - V. L. Ermolaev and E. B. Sveshnikova, Izv. Akad. Nauk SSSR Ser. Fiz. **26**, 29 (1962) [V. L. Ermolaev and E. B. Sveshnikova, English transl.: Bull. Acad. Sci. USSR Phys. Ser. **26**, 29 (1962)].

of the fluorescent. However, to the best of our knowledge, this mechanism of energy transfer from the excited states of organic phosphors to fluorescent acceptors wasn't explored further for construction of efficient OLEDs. In 2019, Reineke and collaborators reported the observation of singlet-singlet and triplet-singlet intermolecular Förster-type resonant energy transfer (FRET) from a biluminescent donor molecule, showing simultaneous fluorescence and phosphorescence at room temperature, to a single fluorescent acceptor dispersed in an amorphous polymeric film.[21]

During the last decade some of us have published on a series of organic tandem luminophores (ARC-Lum probes) that upon excitation with a flash of UV-radiation possess microsecond-timescale photoluminescence if the probe is bound to the active site of a protein kinase.[19,22–25] ARC-Lum probes comprise an organic donor phosphor and an acceptor fluorescent dye covalently linked through a peptidic linker. It was demonstrated that efficient energy transfer from the excited triplet state of the donor to the singlet state of the acceptor fluorophore was responsible for the strong delayed fluorescence with microsecond-range lifetime of the tandem luminophores. However, all previously constructed ARC-Lum compounds possessed complex chemical structures having long peptidic linkers between the chromophores. Therefore, their synthesis in large scale is problematic.

In this work we demonstrate that the non-radiative triplet to singlet energy transfer mechanism is effective even in a simple and easily synthesized metal-free D-A-D molecule. The compound investigated in this work, **ARC-1467**, is made up from two thiophene-comprising donors covalently linked to one perylene bisimide acceptor dye. The thiophene-comprising donor luminophores possess both phosphorescence and weak fluorescence that overlap with the absorption of the perylene bisimide acceptor.

Energy transfer from the excited singlet and triplet states of the donors to the singlet state of the acceptor in **ARC-1467** is thus able to proceed in an intramolecular way in solution and solid films, even without using a metal centre in the donor unit.[21,26]

Experimental

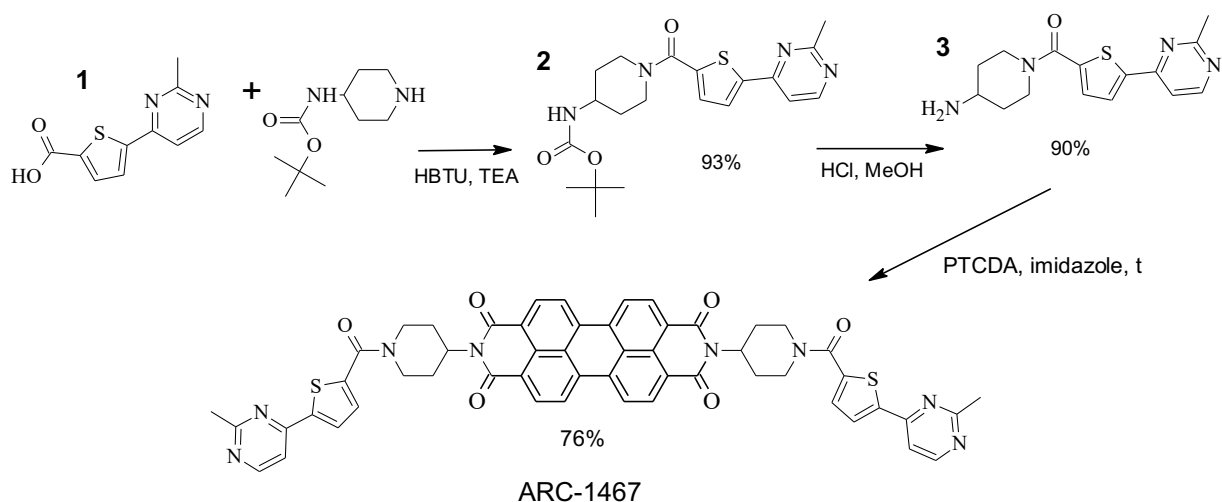
Photophysics. Absorption spectra of 10^{-5} M solutions of compounds were recorded with UV-3600 double beam spectrophotometer (Shimadzu). Photoluminescence (PL) spectra of 10^{-5} M solutions and films were recorded using a FluoroMax-3 or Fluorolog fluorescence spectrometers (Jobin Yvon). Phosphorescence, prompt fluorescence (PF) and delayed fluorescence (DF) spectra, and fluorescence decay curves were recorded using nanosecond luminescence gated acquisition, which allows for emission spectra to be recorded from 400 ps to 1 s. Excitation is supplied by either the third harmonics of a high energy pulsed Nd:YAG laser emitting at 355 nm (EKSPLA) or a nitrogen laser emitting at 337 nm. The emission is focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) having sub-nanosecond resolution. PF/DF time-resolved measurements were performed by exponentially increasing the delay and integration time. Temperature-dependent experiments were conducted using a liquid nitrogen cryostat (Janis Research) in nitrogen atmosphere, while measurements at room temperature were recorded in vacuum in the same cryostat. Further details of the iCCD setup and measurements can be found elsewhere.[27]

Results and Discussion

Design and Synthesis. Previously disclosed ARC-Lum probes possessed complex structures and their synthesis followed multiple steps. Usually, one or two HPLC purifications were needed to get only small quantities of pure ARC-Lum compounds.

The final synthesis step was the labelling with an expensive commercially available fluorescent dye. Therefore, only sub-milligram to milligram quantities of ARC-Lum probes were prepared.

Here we report the design and synthesis of the D-A-D luminophore **ARC-1467** (Scheme I), a new compound that could be produced in much larger quantities from inexpensive starting materials. 5-(2-methylpyrimidin-4-yl)thiophene-2-carboxylic acid **1** was selected for the phosphorescent donor fragment due to its strong phosphorescence and relatively weak fluorescence emission in polyvinyl alcohol (PVA) at room temperature.[28] Perylene bisimide was chosen for the acceptor dye because of its high fluorescence quantum yield, low cost, and offered possibility of attaching two donor moieties to a single acceptor.[29] 4-Amino-piperidine was selected as the linker structure used to separate the donor and acceptor moieties, as it is short enough to allow fast FRET to occur. On the other hand, the linker was sufficiently rigid to avoid direct contacts between the donor and acceptor moieties. Coupling of thiophene derivative **1** with Boc-protected 4-amino-piperidine yielded amide **2**. Thereafter, the Boc group was removed by acid treatment, giving amine **3**. Both reactions revealed high yields and the application of simple liquid-liquid extraction was enough to get a pure product. Heating of amine **3** and perylenetetracarboxylic dianhydride in melted imidazole gave **ARC-1467** in 76% yield.



Scheme I – Synthesis of ARC-1467.

Photophysics. The absorption and fluorescence spectra of **ARC-1467** are shown in **Figure 1a**, together with the absorption, fluorescence, and phosphorescence spectra of the distinct donor unit. The absorption spectrum of **ARC1467** is basically compiled from the sum of the donor and acceptor absorptions, giving indication that no additional ground-state complex is formed (see ESI point 2). The fluorescence of the distinct donor unit is very weak, peaking around 400 nm, consistent with its high ISC yield. In contrast with the weak fluorescence, the phosphorescence observed at 80 K is strong, peaking at around 550 nm (see ESI point 2). The acceptor dye shows well-resolved intense fluorescence, as it is typical for many perylene derivatives. Importantly for the occurrence of triplet-to-singlet energy transfer, the phosphorescence of the donor molecule largely overlaps with the absorption of the acceptor unit.[21]

The photoluminescence emission spectra of **ARC-1467** match the fluorescence of the acceptor showing that no charge transfer is taking place between the donor and acceptor units. No donor emission is observed in the **ARC-1467** spectrum,

independently of the excitation wavelength showing that the rates of donor emission (fluorescence or phosphorescence) cannot outcompete with the energy transfer rate to the acceptor. The energy of the singlet excited state of the single donor unit ($S_1^D = 3.8 \text{ eV}$) is determined from the onset of the respective fluorescence spectrum. **ARC-1467** emits at lower energy as it fluoresces from the singlet state of the acceptor only ($S_1^A = 2.4 \text{ eV}$). Similarly, the energy of the triplet state of the donor unit is determined from the onset of the donor phosphorescence ($T_1^D = 2.6 \text{ eV}$).

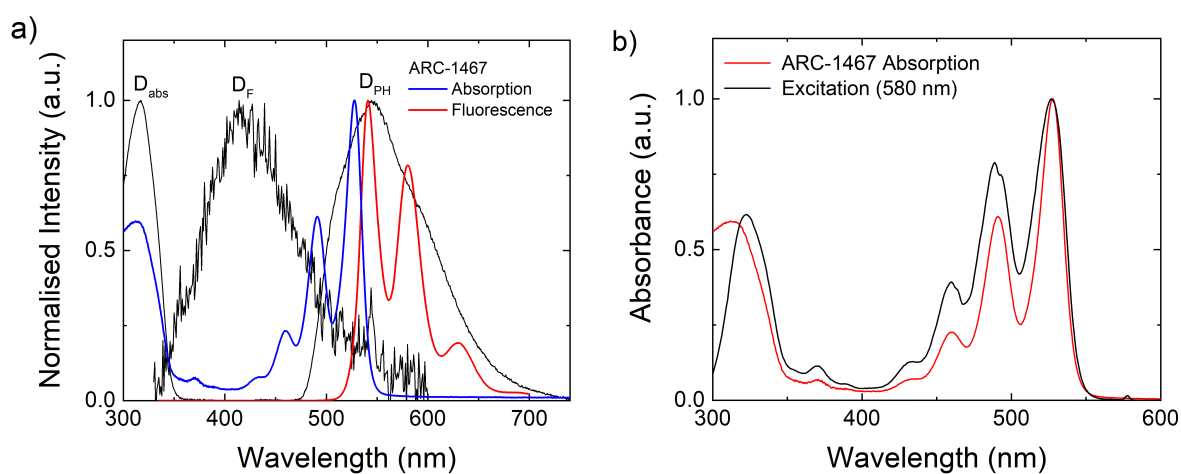


Figure 1 – a) Absorption (blue) and fluorescence (red) spectra of **ARC-1467** with excitation at 325 nm in chloroform. Donor absorption and fluorescence in chloroform, with excitation at 325 nm, and phosphorescence collected at 80 K in polystyrene, with $\lambda_{\text{ex}} = 337 \text{ nm}$ (all black). b) Absorption (red) and excitation (black) spectra of **ARC-1467** with emission collected at 580 nm in chloroform.

The absorption and excitation spectra of **ARC-1467** in chloroform are compared in **Figure 1b**. The excitation spectrum collected at the acceptor emission ($\lambda_{\text{em}}=580 \text{ nm}$) reproduces well the absorption of both the donor and acceptor units, showing that the donor unit contributes to the **ARC-1467** fluorescence through energy transfer. Owing to the strong overlap between the fluorescence and phosphorescence spectra of the donor and the absorption spectrum of the acceptor, FRET can occur in **ARC1467**

directly from both the singlet (S_1^D) and the triplet (T_1^D) state of the donor to the singlet state of the acceptor (S_1^A).[21,26] However, no evidence has been found for the occurrence of direct triplet-triplet energy transfer ($T_1^D \rightarrow T_1^A$). This is in line with previous observations[21] and it is also consistent with the expected attenuation effect on the non-radiative triplet-triplet energy transfer rate introduced by the bridge, as triplet-triplet energy transfer mostly occurs by the Dexter mechanism.[30] Moreover, the triplet state of perylene (~ 1.53 eV),[31,32] is at much lower energy than the triplet energy of the donor unit, ($T_1^D = 2.6$ eV), which most probably contributes also to make $T_1^D \rightarrow T_1^A$ transitions unlikely to compete with $T_1^D \rightarrow S_1^A$ transfer.

The photoluminescence quantum yield (PLQY) of **ARC-1467** in chloroform solution measured with excitation in the acceptor unit is close to 100%. However, when dispersed in a thin polystyrene film the PLQY is significantly reduced even at very low concentration, and it decreases even further if the concentration is increased. This is probably due to the formation of aggregates involving π - π^* stacking of perylene moieties that enhance non-radiative decay processes. Therefore, to minimize luminescence quenching due to aggregation, we have measured the PLQY of **ARC-1467** in drop-cast films, prepared with 0.005 % w/w of the compound dispersed in polystyrene, obtaining the PLQY of 31 ± 6 %.

The occurrence of $T_1^D \rightarrow S_1^A$ energy transfer was confirmed by time-resolved methods (see also ESI point 3). **Figure 2a** shows the photoluminescence decay of **ARC-1467**, obtained with excitation at the very edge of the donor absorption ($\lambda_x=355$ nm), in deoxygenated chloroform solution at RT. The photoluminescence shows two temporally distinct decay regions. A fast component, decaying with 4.9 ns lifetime, is consistent with excitations formed through rapid $S_1^D \rightarrow S_1^A$ energy transfer, and

potentially also due to direct excitation of the acceptor. This fast decay is then followed by a slower signal component, decaying with $5.7 \mu\text{s}$ lifetime, appearing as a result of $T_1^D \rightarrow S_1^A$ energy transfer. **Figure 2b** shows the phosphorescence decay of the single donor unit measured in polystyrene at 80 K. In the absence of other processes, the excited triplet state of the isolated donor molecule shows a lifetime of 69 ms, compared to the microsecond-scale luminescence lifetime of **ARC-1467** delayed fluorescence. This result confirms that the observed delayed fluorescence is not the result of simple radiative energy transfer caused by the reabsorption of the emitted donor phosphorescence.

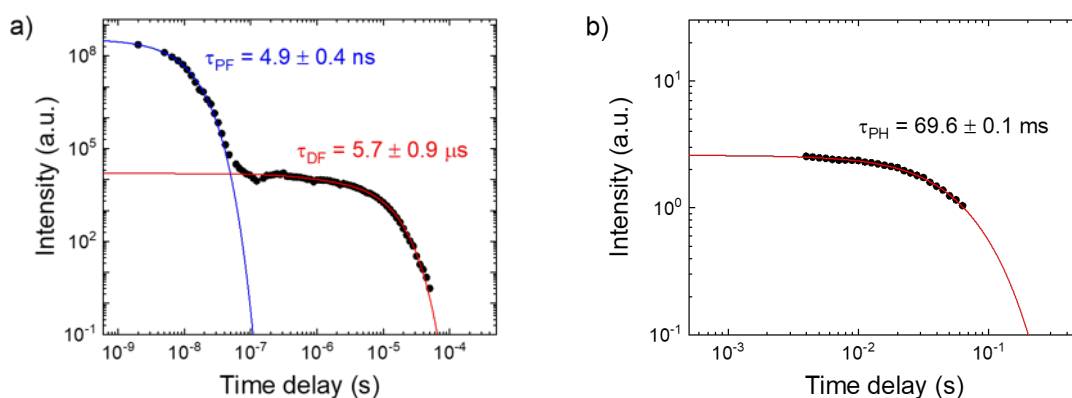


Figure 2 – a) Fluorescence decay of **ARC-1467** in deoxygenated chloroform, excited at the D unit ($\lambda_x=355 \text{ nm}$) at RT; b) phosphorescence decay of the distinct D unit, collected in polystyrene at 80 K.

The interpretation of the fluorescence decay data is further confirmed in **Figure 3**, showing the time-gated fluorescence spectra of **ARC-1467** dispersed in polystyrene, collected with excitation at the donor unit ($\lambda_x = 355 \text{ nm}$) and directly exciting the acceptor unit at $\lambda_x = 532 \text{ nm}$.

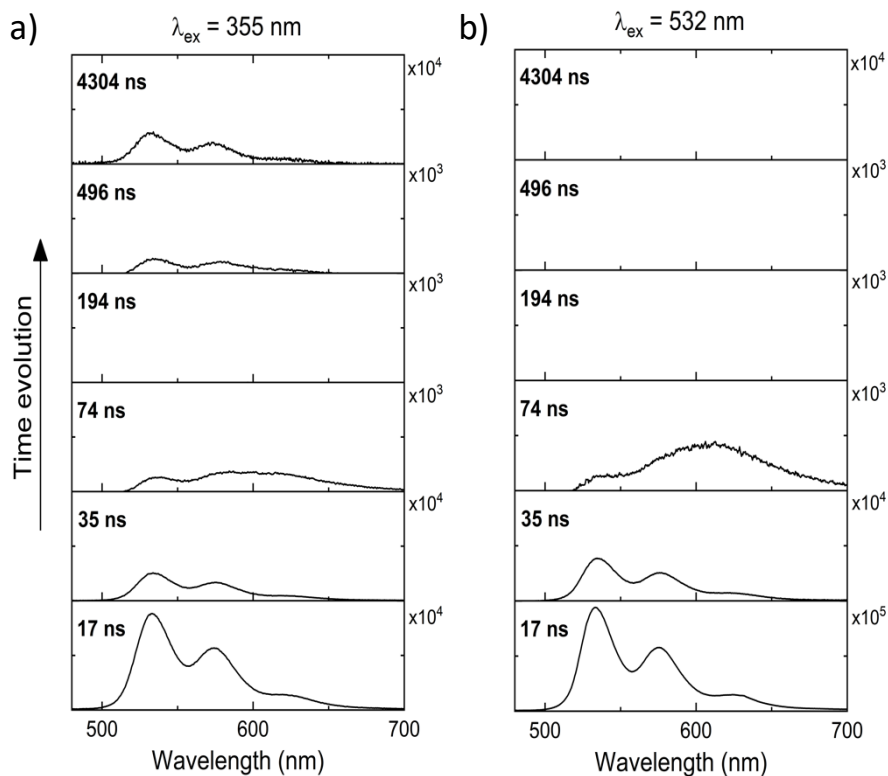


Figure 3 –Time-evolution of light emission of **ARC-1467** in polystyrene at RT a) under excitation on the D ($\lambda_{ex}=355$ nm) and b) excitation on the A ($\lambda_{ex}=532$ nm).

Figures 3a and **3b** show the time evolution of **ARC-1467** emission spectra, i.e., time-resolved spectra obtained at different delay times following excitation in the donor and acceptor units, respectively. Prompt (PF) and delayed (DF) fluorescence components with the same perylene-like emission spectrum are observed when the excitation occurs in the donor absorption region. However, when the excitation occurs in the acceptor region no delayed perylene emission is detected. In both cases, i.e., either with 355 nm or 532 nm excitation, a weak broad emission is observed following the decay of the prompt fluorescence (4.9 ns delay time). We attributed this spurious emission due to the formation of aggregates in the polystyrene film, which is entirely consistent with the well-known tendency of perylene derivatives to form aggregates in solid state.[29]

The relative contributions of PF and DF can be determined from the decay represented in Figure 2a, using eq. 1, where A_{PF} and A_{DF} represent the pre-exponential amplitudes associated with the PF and DF decays, and τ_{PF} and τ_{DF} are the PF and DF decay times, respectively, giving a DF/PF ratio of 0.058. Thus, in **ARC-1467** 6% of all absorbed photons are transferred from the triplet to the singlet state and contribute to delayed fluorescence.

$$\frac{\int DF}{\int PF} = \frac{A_{DF}\tau_{DF}}{A_{PF}\tau_{PF}} \quad (1)$$

The yield of perylene bismides singlet states formed *via* the triplet to singlet energy transfer path can be estimated from eq. 2. In this equation, $\Phi_T^{D/A}$ represents the triplet formation yield in **ARC-1467** – *i.e.*, when the donor unit is in presence of the acceptor unit – $\Phi_{ET}^{D^T-A^S}$ represents the yield of energy transfer between the excited triplet state of the donor and the singlet state of the acceptor, $\Phi_{ET}^{D^S-A^S}$ is the yield of energy transfer between the excited singlet state of the donor and the singlet state of the acceptor, and α accounts for the possibility of direct excitation of the acceptor.

$$\frac{\int DF}{\int PF} = \frac{\Phi_T^{D/A}\Phi_{ET}^{D^T-A^S}\Phi_f^A}{(\Phi_{ET}^{D^S-A^S} + \alpha)\Phi_f^A} = \frac{\Phi_T^{D/A}\Phi_{ET}^{D^T-A^S}}{(\Phi_{ET}^{D^S-A^S} + \alpha)} \quad (2)$$

Assuming $\Phi_{ET}^{D^S-A^S} + \Phi_T^{D/A} \approx 1$, as no donor fluorescence is observed in the complex, eq. 3 gives the upper limit (internal conversion is neglected) for the yield of $T_1^D \rightarrow S_1^A$ energy transfer.

$$\Phi_{ET}^{D^T-A^S} = \frac{(1 + \alpha - \Phi_T^{D/A})}{\Phi_T^{D/A}} \frac{\int DF}{\int PF} \quad (3)$$

The relatively small yield of perylene singlet excited states formed via the triplet-to-singlet energy transfer path in **ARC-1467**, just ~6 %, if compared with the PF contribution of ~94 %, is consistent with the expectation that the rate of singlet-singlet energy transfer is much faster than the rate of ISC of the donor unit. Therefore, the triplet formation yield in the complex must be very small and this is the step limiting the efficiency of the mechanism (under optical excitation). However, as the yield of triplet state formation in the donor, $\Phi_T^{D/A}$, increases - triplets are formed in great numbers - the first factor on the right side in eq. 3 tends to α , and the DF/PF ratio is maximum, since PF decreases, and DF must increase. In this situation the contribution of $T_1^D \rightarrow S_1^A$ energy transfer would be at its maximum. In other words, the yield of triplet to singlet energy transfer in **ARC-1467** is small (~6%) relatively to the total excited state population, however if measured relatively to the triplet population of the donor, the fraction of triplets that are converted into singlet states of the acceptor may be close to 100%, *i.e.*, every triplet state formed in **ARC-1467** is able to be transferred to the singlet state of the acceptor unit.

As the delayed emission is originated from the triplet state of the donor through energy transfer to the singlet state of the acceptor, and the singlet state of the acceptor is much shorter lived than the donor triplet state, the lifetime of the delayed fluorescence is equal to the lifetime of the donor triplet state in the presence of the acceptor. The efficiency of the triplet-to-singlet energy transfer step can thus be estimated using the phosphorescence lifetime of the isolated donor (69.6 ms) and the lifetime of the delayed fluorescence (0.0057 ms), both determined in polystyrene at 80 K, giving $E = 1 - \frac{\tau_{DA}}{\tau_D} \cong 1$. This result is highly significant since in applications using electroluminescence, such as in OLEDs, where the triplet yield is constantly at 75%,

the contribution of triplet-singlet energy transfer will be predominant, justifying the relevance of our results as a proof of concept.

The intensity of delayed fluorescence increases linearly with excitation power in a logarithmic representation (see ESI 3). This power dependence confirms that the delayed fluorescence results from a pure intramolecular mechanism.

Finally, we sought to understand how temperature could affect the $T_1^D \rightarrow S_1^A$ energy transfer process. As the singlet state of the acceptor unit is at lower energy than the triplet state of the donor the energy transfer should proceed regardless of temperature (assuming no energy barrier is involved in the mechanism). Fluorescence decays of **ARC-1467** dispersed in polystyrene obtained with excitation on the donor unit, thus showing the PF and DF components, were collected between 295 K and 80 K (see ESI point 3). As expected, no variation of the DF/PF ratio and DF lifetime is observed between room temperature and 80 K. As we have established above that the DF lifetime is equal to the lifetime of the donor triplet state in presence of the acceptor, the independence of the DF lifetime with temperature, shows that the rate of triplet-singlet energy transfer must be much faster than the rate of triplet decay directly to the ground state. Otherwise, the DF lifetime would have to increase with decreasing temperature due to the non-radiative decay of the donor triplet state being suppressed at low temperature. The rate of triplet-singlet energy transfer in **ARC-1467** can thus be estimated as $k_{ET}^{T \rightarrow S} = \tau_{DF}^{-1} \approx 1.7 \times 10^5 s^{-1}$.

The mechanism describing the energy transfer pathways available in **ARC-1467** is finally represented in Figure 4.

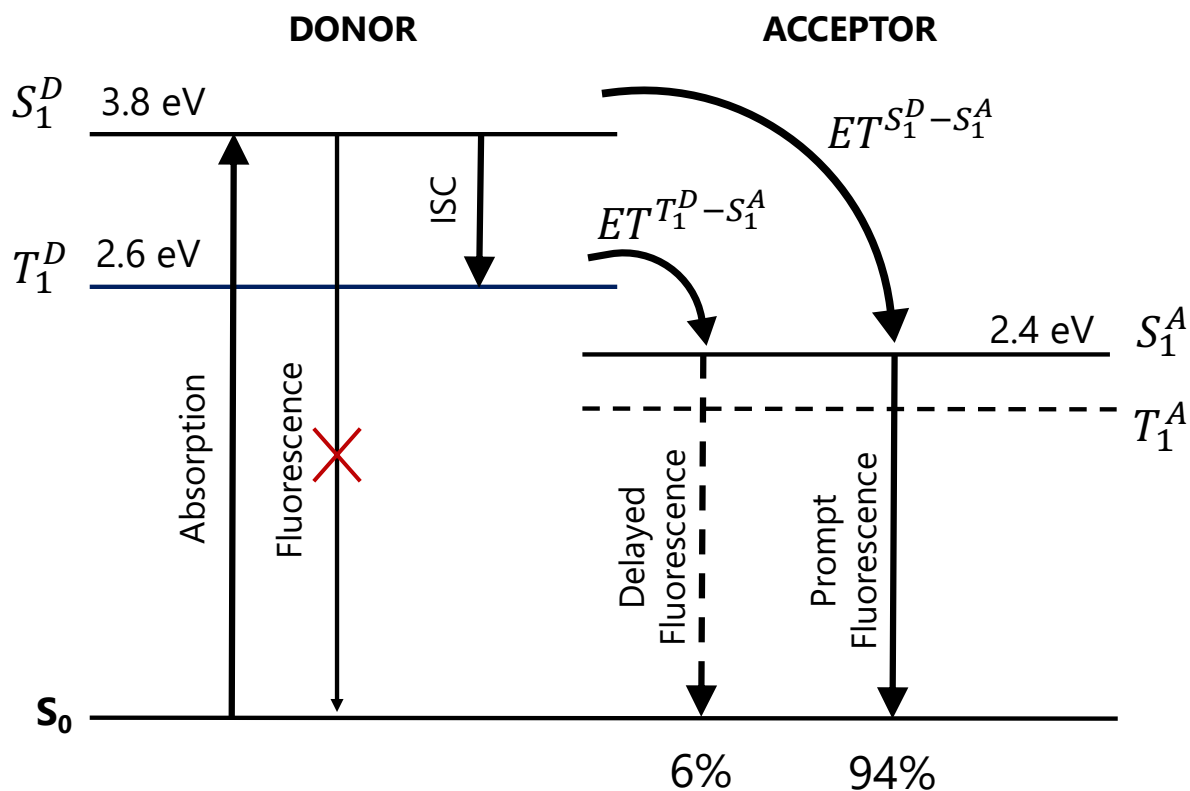


Figure 4 – Schematic diagram representing the energy transfer mechanism in ARC-1467 luminophore.

Conclusions

In summary, the intramolecular energy transfer from the excited triplet state of the donor unit to the singlet state of an acceptor with bright fluorescence $T_1^D \rightarrow S_1^A$ is demonstrated for the metal-free D-A-D molecule **ARC-1467** in solution and in solid films where the compound is dispersed in polystyrene. In **ARC-1467** the donor and acceptor units are separated by a rigid bridge, therefore the $T_1^D \rightarrow S_1^A$ energy transfer is likely to occur through nonradiative dipole-dipole interactions following the FRET mechanism. This mechanism is evidenced by the shorter, 5.7 μs lifetime of delayed fluorescence of the acceptor dye, if compared to the millisecond-range lifetime of the triplet state of the single donor unit.

Conflicts of interests

There are no conflicts of interest to declare.

Acknowledgments

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