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Energy Upconversion via Triplet Fusion in Super Yellow PPV Films Doped with Palladium Tetraphenyltetrabenzoporphyrin: a Comprehensive Investigation of Exciton Dynamics

Vygintas Jankus, Edward W. Snedden, Daniel W. Bright, Victoria L. Whittle, J. A. G. Williams, and Andy Monkman*

One of the key issues concerning the development of efficient polymer solar cell technology is the lack of viable materials which absorb in the near-infrared (NIR) region. This could be resolved by up-converting energy from the NIR into visible using triplet fusion (TF) with an additional layer that is fabricated separately from the solar cell and deposited on top. Theoretically a maximum upconversion (UC) via TF efficiency of 50% could be obtained. Here, it is demonstrated that in a film of commercially available poly(para-phenylene vinylene) copolymer "super yellow" (SY) doped with 4% palladium(*meso*-tetraphenyl-tetrabenzoporphyrin) (PdTPBP) sensitizer, an UC efficiency of 6% can be achieved. By using femtosecond and nanosecond spectroscopies it is shown that the main UC efficiency loss mechanism is due to triplet quenching in PdTPBP aggregates. The PdTPBP intersystem crossing rate constant is determined to be 1.8×10^{11} s^{-1} and the triplet energy transfer rate constant from PdTPBP to SY to be 10^9 s^{-1}. Quenching in PdTPBP aggregates can account for a triplet concentration loss in the range of 76-99%. As such, preventing sensitizer aggregation in NIR-to-visible upconverting films is crucial and may lead to substantial increase of UC efficiencies in films.

1. Introduction

In recent years the research literature on polymer solar cells (PSC) has increased considerably.[1–5] This technology is especially attractive due to the ease of processing, mechanic flexibility and the possibility of processing polymer solar cells as large area panels using roll-to-roll, inkjet printing or slot coating technologies. Unfortunately, the present power conversion efficiencies of PSCs are still too low and need to be enhanced. In 1961 Shockley and Queisser[6] proposed that the efficiency of solar cells depends on the band gap of the reactive material. This is a direct consequence of the fact that photons of lower energy than the semiconducting band gap cannot be absorbed, while charges created after absorption of photons of higher energy than the band gap, undergo thermalization. In organic solar cells donor and acceptor molecules are used and charge transfer between them occurs at an approximate minimum 0.3 eV difference between the lowest unoccupied molecular orbital (LUMO) of donor and LUMO of the acceptor. Experiments also show that the open circuit voltage of the cell is reduced by a further 0.3 eV, the origins of which is still under discussion,[5,7,8] giving a total loss of 0.6 eV. In addition, transport losses and other efficiency restrictions have to be considered and, based on these assumptions, Ameri et al. estimated that the maximum achievable efficiency of PSCs is ≈11% for a donor having a band gap of 1.5 eV and ideal LUMO difference of 0.3 eV.[5]

Unfortunately PSCs absorb very weakly in the red and near-infrared (NIR) regions, in contrast to their inorganic counterparts. For example, the most popular polymer solar cell material blend poly(3-hexylthiophene): phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM), has a maximum absorption at ≈515 nm and band edge is at 650 nm (see, e.g., ref. [1–5]). The photon flux of solar radiation falling in the region 450–650 nm is 8.3×10^{20} photons s^{-1} m^{-2} nm^{-1} whereas for the 650–850 nm region it is 8.5×10^{20} photons s^{-1} m^{-2} nm^{-1} (**Figure 1**). These are nearly equal: shifting PSC absorption into the NIR region is therefore crucial to obtain high-efficiency solar energy conversion. Fabricating tandem cells[5] or tuning the absorption band of the polymer further to the red[9] have been proposed but both methods have drawbacks. In the former case fabrication becomes overcomplicated and in the latter case losses would be unavoidable due to the reduction in open-circuit voltage and loss of absorption in the UV/blue region.[8,10]

Dr. V. Jankus, Dr. E. W. Snedden, Dr. D. W. Bright, Prof. A. Monkman
Physics Department
University of Durham
South Road, Durham, DH1 3LE, UK
E-mail: vygintas.jankus@durham.ac.uk
Dr. V. L. Whittle, Dr. J. A. G. Williams
Chemistry Department
University of Durham
South Road, Durham, DH1 3LE, UK

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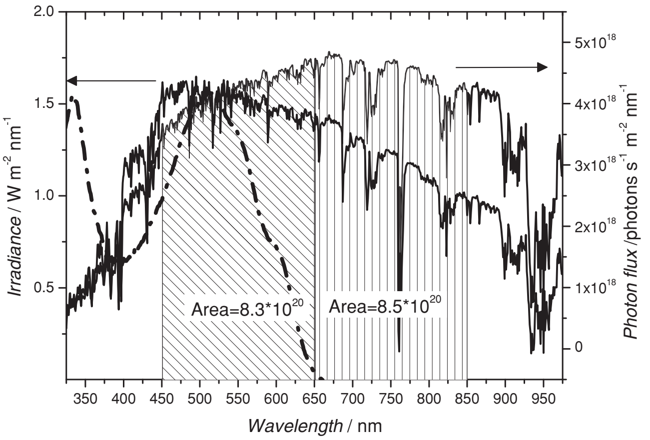

Figure 1. Irradiance and photon flux spectra of solar radiation reaching the Earth's surface. Areas from 450 to 650 nm and from 650 to 850 nm are indicated by diagonal and vertical striped shading respectively. For comparison, an appropriately scaled absorption spectrum of P3HT:PCBM, a material widely used in PSCs, is also included (dashed line).

Another way of solving this problem would be by up-converting energy from the NIR to the visible using triplet fusion (TF)[11–14] with the help of an additional single layer which could be fabricated separately from the solar cell and deposited on top (**Figure 2**). This layer consists of a sensitizer to absorb NIR photons that creates singlet states which then undergo rapid intersystem crossing (ISC) to the triplet manifold. Ideal sensitizers are heavy metal complexes which have very rapid ISC and triplet yields close to 100%.[15] From the sensitizer triplet level, energy is then transferred via the Dexter mechanism to the triplet level of the host.[16] Theoretically, 100% efficiency can be achieved here if the triplet level of the sensitizer is higher than that of the host and all sensitizer molecules are in close contact to acceptor molecules. This means that preferably the triplet level of the host should be of the order of 10500 cm^{-1} (equivalent to 950 nm) if NIR absorption between 650–850 nm is to be used. The next step after energy transfer is the fusion of two triplet excitons in the host to create higher energy singlet excitons i.e., photon upconversion (UC). These singlet states then emit (in the visible) and the light is reabsorbed by a conventional PSC. Triplet fusion in the host is highly desirable whereas in the sensitizer it should be avoided. Any thickness of the upconverted layer can be deposited on the solar cells as upconversion process is not limited by charge mobility. For instance, films of 1 µm thickness or more could be slot-coated on top of the solar cell which is a very easy and cheap process. Up-conversion via TF in photoelectrochemical cells has also been explored, work still in its infancy and alternatives such as proposed above are desirable.[17,18] The question arises, how efficient can the TF process be in reality?

Simple spin statistics predict that the triplet fusion process should be 5.5% efficient: i.e., the efficiency of creating one singlet exciton from one triplet exciton is 1 in 18:[19]

$$ {}^{3}A^{*} + {}^{3}A^{*} \longrightarrow \begin{cases} 1/9\,{}^{1}(AA)^{*} \longrightarrow {}^{1}A^{*} + {}^{1}A \\ 1/3\,{}^{3}(AA)^{*} \longrightarrow {}^{3}A^{*} + {}^{1}A \\ 5/9\,{}^{5}(AA)^{*} \longrightarrow {}^{3}A^{*} + {}^{1}A \end{cases} \tag{1} $$

where $^1A^*$ and $^3A^*$ are excited singlet and triplet states and $^1(AA)^*$, $^3(AA)^*$, $^5(AA)^*$ are interaction pairs with singlet, triplet, and quintuplet spin multiplicities, triplet fusion being the channel which yields a singlet state, this though ignores singlets produced by triplet recycling as explained below.

However, recent experimental evidence suggests that this value could be higher. For example, Schmidt et al.[20] estimate it to be at least double at 12.5%. More recently using organic light emitting diodes (OLED), Kondakov et al. have inferred an efficiency for this process of 20%.[21,22] They rationalize their results by assuming that quintuplet states are energetically unfeasible and lead to scattering, such that the only annihilation products are singlets or triplets. When triplet recycling is taken into account, i.e., the fact that a triplet left after annihilation can interact again with another triplet to form a singlet until all triplets are used up, the predicted singlet yield becomes $\sum_{n=0}^{\infty} \frac{13^n}{18^n+1} = 0.2$. Furthermore, by an indirect experiment using OLED measurements, the same group recently calculated that 50% triplet-to-singlet conversion efficiency in rubrene has being achieved.[23] The explanation for this comes from the fact that the combined energy of two triplets in rubrene is lower than the energy of the next available T_N level and so this cannot be reached energetically. Consequently, the only path for triplet relaxation is triplet fusion via the singlet channel and all triplets can be used to create singlets with a yield of 0.5,[23] if triplet internal conversion is very slow. Hence, if properly designed, such an NIR upconverter could increase solar cell efficiency by 50%, assuming a host fluorescence quantum yield of 1 and that the sensitizer-to-host transfer efficiency is 1. This implies that a new design of solar cells with an NIR upconverter could greatly enhance the efficiency of PSCs using simple, well-understood P3HT:PCBM cells.

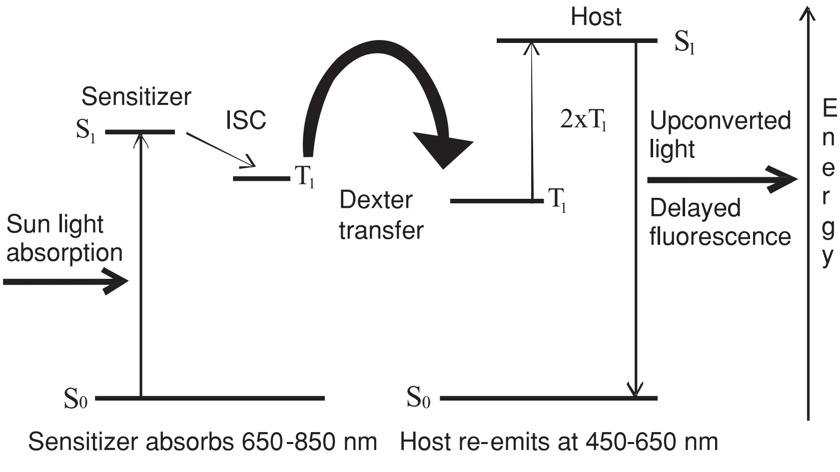

Figure 2. Jablonski diagram of NIR upconversion (UC) via triplet fusion. The proposed system consists of host and sensitizer to be deposited on the top of the polymer solar cell. Requirements: triplet yield of the sensitizer ≈ 100%; E(S$_1$) sensitizer < E(S$_1$) host; E(T$_1$) sensitizer > E(T$_1$) host

Upconversion via tripelt fusion has already been demonstrated in a few solution-based systems consisting of host and sensitizer[12–14,24,25] and, although these studies have uncovered some of the physics of these systems, they are not very applicable to commercial polymer solar cells. It is important to note here that, in solution, upconversion via triplet fusion can be achieved using non-coherent light.[12] This is possible because the triplets live for a very long time and illumination with a continuous wave (CW) source generates a high equilibrium population which later can fuse and generate singlets. Energy upconversion via triplet fusion in films has also been shown but only to upconvert green photons to blue: it could not be extended into the NIR region due to the high triplet level of the host.[26] Small molecules with appropriate triplet levels are available but, if used in the solid state, they need to be doped into an inert spin-coatable matrix such as cellulose acetate or rubbery polymer.[27–29] This complicates fabrication and phase separation is more probable which would lead to subsequent aggregation and quenching of triplets in lower lying aggregate sites. Furthermore, this could reduce the efficiency of TF due to the larger separation between triplet excitons and very poor triplet mobility between active sites resulting in lower triplet densities. Clearly the biggest handicap to moving forward in applying this concept to real PSC is the absence of an easily spincoatable active host material. Here we show for the first time that NIR-to-visible upconversion in a spin-coatable polymer film can be achieved, which is the first step towards the application of this concept in solar cells and further development. We point out here, that although in this paper we use dopant absorbing in deep red the polymer host system under investigation due to its low triplet level has a capacity to host dopants with triplet levels up to 950 nm (see below).

In this paper we demonstrate upconversion via triplet fusion in a readily accessible, commercial, spin-coatable poly(para-phenylene vinylene) copolymer, "super yellow", (SY).[30] The emission spectra of SY peaks at 561 nm, overlapping well with the absorption of the widely used PSC material, P3HT:PCBM (**Figure 3**). The absorption peak of SY is at 450 nm (P3HT:PCBM at 512 nm) and can also function as an energy down-converter compensating for the weaker absorption of P3HT:PCBM in the deep blue region. We employ steady state, nanosecond and femtosecond spectroscopies to investigate the exciton dynamics in 4% PdTPBP:SY films, with a goal to understand triplet exciton dynamics in these blends and to determine the dominant efficiency loss mechanism.

2. Results and Discussion

2.1. Steady State

Spectroscopic characterization of SY is shown in Figure 3. The photoinduced triplet-triplet absorption (SY TA) spectrum of SY film was recorded at 80 K and displays peaks at ca. 833 nm (Figure S3 in the Supporting Information). Unfortunately, phosphorescence spectra have never been recorded from the PPV family of polymers, including SY. There is only one report where phosphorescence of a PPV derivative is claimed to have been recorded with the help of Pt(II) octaethylporphine (PtOEP) as a triplet sensitizer.[31] However, this emission is the same as that recorded from PtOEP aggregate reported by Leo et al.[32] We have also tried to record SY phosphorescence by isolating it in zeonex (to reduce triplet migration), by using triplet sensitizers such as PtOEP or PdTPBP (to increase the triplet population) and by using degassed iodotoluene solution at low temperatures (in an attempt to increase the spin-orbit coupling and triplet formation yield and to promote the $T_1 \rightarrow S_0$ radiative decay), but with no success. Nevertheless, the triplet properties of SY can be inferred from those of poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene-vinylene] (MEH-PPV), since SY consists of MEH-PPV moieties. The triplet level of MEH-PPV has been determined using pulse radiolysis energy transfer.[33] Indeed the peak of SY triplet absorption at 833 nm (1.49 eV) recorded by us (T_1-T_N gap) coincides very well with the T_1-T_N gap of MEH-PPV (1.5 eV or 827 nm).[33] Consequently the triplet energy of SY should be similar to that of MEH-PPV, which is 1.3 eV (953 nm). This means that SY, like MEH-PPV, has $2xT_1 < T_N$ giving rise to the possibility of upconverting triplets with 50% efficiency. This is also true for other members of the PPV family of polymers such as poly(2,5-hexyloxyphenylenevinylene) (DHOPPV) and poly(2,5-octyloxyphenylenevinylene) (DOOPPV), $2xT_1<T_N$.[33] The absence of phosphorescence could be explained by the bandgap law, with a decrease of bandgap non-radiative decay rate should increase exponentially.

PdTPBP has a singlet level at 1.85 eV (λ = 669 nm)[15] which is at lower energy than the singlet of SY (2.21. eV, 561 nm), as required for upconversion. The triplet yield of this sensitizer

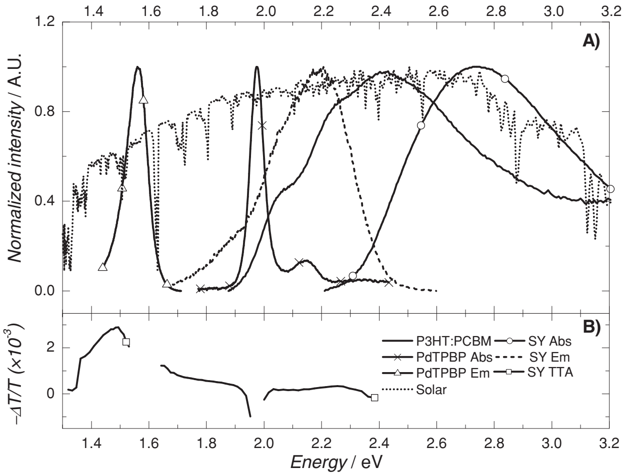

Figure 3. A) Summary of the optical spectra of the various components under investigation: absorption and emission spectra of SY and PdTPBP. Emission spectrum of SY was recorded from 4% PdTPBP:SY film 300 ns after excitation at 1.96 eV into the Q band of PdTPBP. The AM1.5 solar spectrum (black) and the absorption spectrum of RR-P3HT:PCBM (1:1 wt%) (bulk-heterojunction blend) have also been included for reference. B) Photoinduced absorption spectrum of SY:PdTPBP (1:0.04 wt%) blend film at 10 μs. A broad absorption (onset ≈1.4 eV) is attributed to the triplet-triplet absorption of SY; note that the tail of the absorption appears to extend to energies as high as 2.4 eV. A weaker absorption peak (onset ≈2.2 eV) can be just resolved and is attributed to the triplet-triplet absorption of PdTPBP. Photobleaching of the PdTPBP ground-state absorption is also observed at 1.95 eV. Data has been rejected in the vicinity of 1.6 eV and 1.97 eV due to saturation from residual 1.6 eV light in the white-light probe and scatter from the excitation line, respectively.

is 97%[12] and the triplet energy is 1.57 eV, which is higher than that of SY at 1.3 eV. If doped with 4% PdTPBP, upconversion via triplet fusion can be achieved in SY. After excitation of a 4% PdTPBP:SY film at 632 nm, emission peaking at 560 nm is observed at late times after excitation (see Figure 3A for spectrum). This emission spectrum recorded 300 ns after excitation is identical to SY film fluorescence observed by us previously.[30] Similar delayed emission spectra after excitation at 632 nm have been observed at various PdTPBP concentrations in SY and at few temperatures (see Supporting Information). We note here that the control experiment would be to excite SY without PdTPBP at 632 nm. The absorption of super yellow is provided in Figure 3A showing zero absorption at this wavelength. Indeed, exciting pure SY film, without PdTPBP dopant, at 632 nm results in zero delayed emission.

2.2. Femtosecond Spectroscopy

Femtosecond transient absorption spectroscopy was employed to investigate the generation of triplet excitons in the PdTPBP:SY film. The transient absorption spectrum of the film at different pump-probe delay times, following selective excitation of the PdTPBP moieties at 1.95 eV, is presented in **Figure 4**. At 0 ps, the spectrum is characterised by strong photobleaching ($\Delta T/T > 0$) of the PdTPBP ground state at 1.95 eV. A broad photoinduced absorption band ($\Delta T/T < 0$) is observed between 1.75 and 2.4 eV and overlaps with the photobleaching. Between 0 and 10 ps the photoinduced absorption is rapidly quenched and is matched by the emergence of a new PA peak at 2.3 eV. This change is most clearly observed by comparing the spectra at 0 and 100 ps; note, for example, the prominent decrease in amplitude at 2.07 eV. Previous studies have assigned the peak at 2.3 eV to be the triplet-triplet absorption (T_1-T_N) of PdTPBP.[15] Note that there is no observable change in the signal amplitude at 2.3 eV, indicating that the decrease of the initial photoinduced absorption band is approximately matched in time and amplitude by the build-in of the triplet absorption at that energy.

PdTPBP is a very effective triplet sensitizer which is characterised by an ISC of 97%.[15] As a consequence, the singlet excitons which are created following photoexcitation are expected to be rapidly lost in the process of forming triplet excitons. Hence we attribute the broad (1.75–2.4 eV) band observed at 0 ps to the photoinduced absorption of singlet excitons (S_1-S_N), which is then quenched, giving rise to the triplet absorption at 2.3 eV on the same timescale. The intersystem crossing process can be quantified in time by measuring the decay of the singlet photoinduced absorption at 2.07 eV. The single-wavelength transient absorption kinetics obtained at this energy is shown in Figure 4B. The decay is characterised by a time constant of 5.7 ± 0.3 ps, obtained by multi-exponential analysis of the complete kinetics (see Table S1 in the Supporting Information for a complete summary of the fitting parameters). This corresponds to an ISC rate constant of 1.8×10^{11} s^{-1} for PdTPBP, which is smaller than that normally expected for complexes where triplet yield is >90%, e.g., many iridium complexes.[34] Nevertheless this smaller intersystem crossing rate is consistent with the fact that palladium metal induces smaller spin orbit coupling reflected in larger triplet decay lifetime reaching tens and even hundreds of microseconds[15] (compare with iridium complexes, for example, in ref. [35]).

Between 10 and 3500 ps another new photoinduced absorption band is observed to build in at 1.6–1.8 eV. This band is distinct from both the singlet and triplet absorptions of the PdTPBP and can be most clearly observed in the vicinity of 1.7 eV. The shape of this band matches closely the 10 µs spectrum of SY (Figure 3B) in the same spectral region, indicating the formation of a very long-lived state. The 10 µs spectrum of SY in Figure 3B was recorded by exciting 4% PdTPBP:SY film at 1.96 eV into the Q band of triplet sensitizer PdTPBP. The peak of the long-lived PA in Figure 3B (1.5 eV) is identical to the triplet-triplet absorption energy of the PPV derivative MEHPPV, as reported by Monkman et al.[33] and SY triplet-triplet absorption spectrum (see Supporting Information Figure S3). We thus identify this photoinduced absorption to be the triplet-triplet absorption of SY.

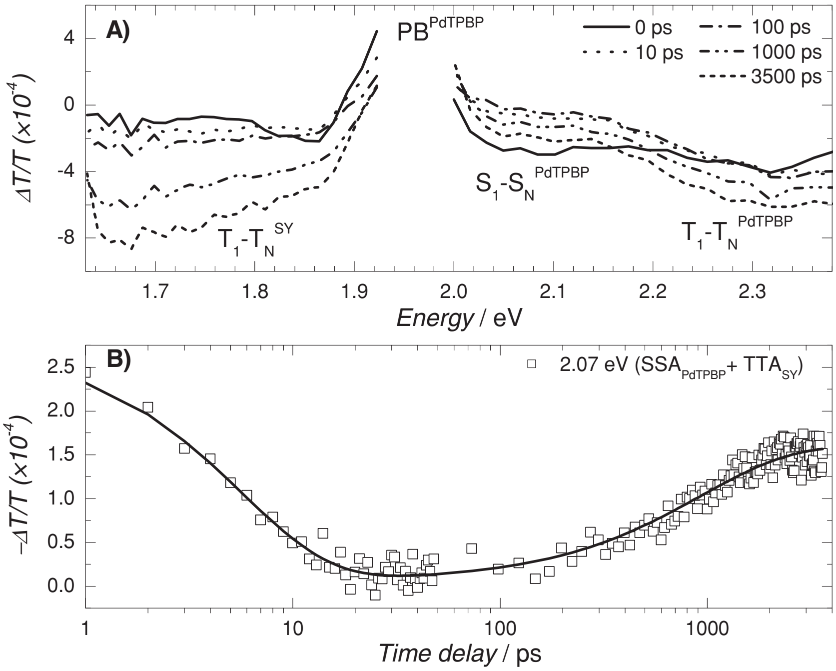

Figure 4. A) Transient absorption spectrum of the PdTPBP:SY (1:0.04 wt%) film, measured at different delayed times (as marked); excitation at 1.95 eV (2 µJ cm^{-2}), 295 K. Bands corresponding to the triplet-triplet (T_1-T_N) absorption and singlet-singlet (S_1-S_N) absorption of the PdTPBP and SY moieties are marked. Data have been rejected in the vicinity of the PdTPBP photobleaching due to scatter from the laser line. B) Single wavelength transient absorption kinetics at 2.07 eV, which contains overlapping contributions from the decay of the PdTPBP singlet absorption and the build-in of the SY triplet absorption. The result of a multiexponential analysis to the data has been included (black line).

Following excitation at 1.95 eV, the formation of triplet excitons in the SY can only arise as a consequence of Dexter energy transfer from the PdTPBP moieties to the SY host. Ideally it would be desirable to measure the decay of the PdTPBP absorption and compare this with the build-in of the SY triplet absorption. Due to the long tail of the SY triplet absorption, however, which extends to energies as high as 2.4 eV, an increase in the photoinduced absorption at 2.3 eV is observed with time. We stress that this does not reflect an increase in the PdTPBP triplet exciton population, but is merely a consequence of the overlap with the triplet absorptions of the SY and PdTPBP moieties; this can be readily appreciated by comparing the build-in at 2.3 eV with the build-in of the SY triplet-triplet absorption at 1.5 eV.

Following on from the above, the tail of the SY triplet absorption is also responsible for the increase in amplitude of the PA at 2.07 eV, as shown in Figure 4B. From the analysis of this data, a time constant of 930 ± 60 ps for the build-in is measured, corresponding to a transfer rate of 10^9 s^{-1}. Given that exciton energy transfer is well established to occur with a lifetime of the order of 10 ps,[30,36,37] the build-in time measured indicates that there is another rate-limiting step regarding the overall transfer of triplet excitons from the PdTPBP into the SY. As the Dexter energy transfer is a short-range "contact" process,[36] the PdTPBP triplet excitons would first be required to migrate to an interface between PdTPBP and SY before transfer could occur. It could not be rejected that triplets are trapped at the interface stabilizing them and slowing down the transfer.[38] However, we propose that the migration and subsequent fusion of triplet excitons in the PdTPBP domains is the rate-limiting process and this has been investigated in more detail using nanosecond spectroscopy and steady state absorption spectroscopy.

2.3. Nanosecond Measurements

Following selective excitation of the PdTPBP moieties at 1.96 eV we recorded and compared the decay of PdTPBP phosphorescence from 4% PdTPBP:SY films, 0.1% PdTPBP:zeonex films, and PdTPBP in degassed toluene. The phosphorescence decay of PdTPBP doped into an inert matrix, zeonex, follows an exponential decay ≈350 μs and the triplet population is effectively constant up to ca. 100 μs as can be visualised in log-log scale (**Figure 5**). Previously Monguzzi et al.[29] recorded PdTPBP lifetime in cellulose acetate to be 280 μs and Rogers et al.[15] recorded it to be 143 μs in pyridine. We recorded the PdTPBP lifetime in degassed toluene to be 280 μs. These differences indicate that the emissive state heavily depends even on the inert environment. However, when doped into SY, PdTPBP phosphorescence decay changes even more dramatically. First of all a fast non-exponential region of decay at initial times is observed (see Figure 5A, squares). PdTPBP phosphorescence decay in SY can be well approximated to the power law with the slope –0.95 (Figure 5B). This slope can be explained by using the classical diffusion equation to describe the triplet dynamics in PdTPBP. We first assume that the triplet concentration on PdTPBP at time 0 is [T] = [T$_0$] which is plausible assumption at timescales of nanosecond spectroscopy. This is then depopulated by monomolecular processes i.e., radiative decay at a rate k_r and non radiative decay rate k_{nr} as well as by bimolecular processes, such as triplet-triplet annihilation (TTA) at a rate k_{tt}:[39–41]

$$\frac{d[T]}{dt} = -(k_{nr} + k_r)[T] - k_{tt}[T]^2 \tag{2}$$

The solution of this equation is[42]

$$[T] = \frac{k_r + k_{nr}}{([k_r + k_{nr}]/[T_0] + k_{tt})e^{(k_r+k_{nr})t} - k_{tt}} \tag{3}$$

where [T] denotes the triplet concentration. If we consider that monomolecular processes are the main mechanism of triplet depletion and that bimolecular process can be neglected, then Equation (2) can be solved to give

$$[T] = [T_0]\exp(-[k_r + k_{nr}]t) \tag{4}$$

If we consider that the radiative lifetime of triplet excitons is very long and if the excitation energy is high leading to triplet dynamics dominated by TTA, then monomolecular processes can be neglected. One can then solve for [T], considering k_{tt} being time-independent, to get

$$[T] = \frac{[T_0]}{(1 + k_{tt}[T_0]t)} \sim t^{-1} \tag{5}$$

Equation (5) shows that if TTA is the dominant decay mechanism in a system, the dependence of the triplet concentration on time (i.e., phosphorescence decay) follows the power law with the slope –1. We indeed get that PdTPBP phosphorescence decays with the slope approaching value –1 when PdTPBP is in a SY host up to ≈150 μs leading to the conclusion that triplet annihilation in PdTPBP is the dominant decay mechanism. This can happen only if molecules are strongly aggregated or are in near

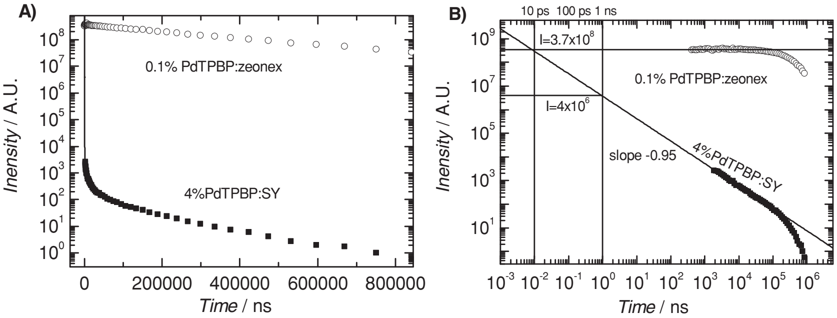

Figure 5. PdTPBP decay from 4% PdTPBP:SY and 0.1% PdTPBP:zeonex films in A) log-lin and B) log-log scales excited at 1.96 eV. Emission from zeonex film is pure exponential indicating absence of triplet-triplet annihilation and energy transfer to the host hence very long decay and almost constant triplet population up to 100 μs (horizontal straight line in B is just a guide to the eye). Emission of PdTPBP from SY film is clearly non-exponential in the initial time region indicating very efficient triplet fusion in PdTPBP or more precisely PdTPBP aggregates. Indeed a power law with slope –0.95 can be fit to this part of decay, which is almost equivalent to Equation 4 characterizing triplet fusion (straight line in A and diagonal straight line in B).

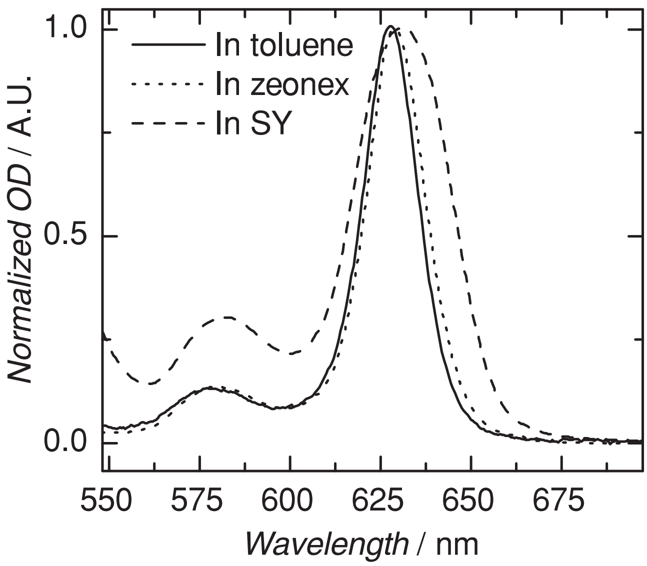

Figure 6. Steady state absorption spectra of 4% PdTPBP:SY, 0.5% PdTPBP:zeonex and PdTPBP in toluene (10^{-6} M). Absorption band of PdTPBP in SY is broader and red-shifted in comparison with PdTPBP in zeonex or toluene indicating aggregation. Note that there is no absorption of SY at this wavelength region (compare to Figure 1).

proximity to each other which is confirmed by absorption spectra (**Figure 6**). When PdTPBP is doped into SY, its absorption band is broader and slightly red-shifted in comparison with absorption band of PdTPBP in zeonex or dissolved in toluene. This happens if molecules are in close proximity to each other or are aggregated which is very likely as PdTPBP is a planar molecule and face-to-face aggregations are highly possible.

Femtosecond measurements show that transfer from PdTPBP to SY is a rate-limiting process (much longer than the Dexter transfer rate, 10^9 s^{-1}); nanosecond gated spectroscopy shows that triplet annihilation in PdTPBP molecules is an additional competing process (PdTPBP phosphorescence follows slope ≈–1 indicating that the dominant process of triplet depletion in PdTPBP is TTA); and steady-state absorption spectra show that PdTPBP molecules aggregate in SY host (absorption band of PdTPBP:SY is broader than that of PdTPBP:zeonex). It all leads to the picture that PdTPBP is aggregated in SY host and that exctions, after intersystem crossing from PdTPBP singlet level to its triplet level, undergo TTA on PdTPBP aggregates. Hence only some of them reach the aggregate boundary and are transferred to SY, whereas others are simply lost during the TTA process on PdTPBP. TTA in PdTPBP aggregates before exciton transfer to SY host will lead to efficiency losses of upconversion via triplet fusion process in 4% PdTPBP:SY films and we can evaluate this semi-quantitatively using the above data.

The triplet transfer from PdTPBP to SY occurs within approximately 1 ns as determined by our femtosecond spectroscopy measurements (see Figure 4B and discussion above). So the majority of triplet excitons will be present on PdTPBP molecules from 10 ps (intersystem crossing rate from PdTPBP singlet to triplet manifold) to 1 ns. Unfortunately we could not record PdTPBP phosphorescence decay at such early times due to the limited time resolution of our nanosecond system and the presence of a long tail of SY singlet emission covering the PdTPBP phosphorescence. At early times the TTA process will completely dominate the dynamics of the system with high exciton density and very little phosphorescence from PdTPBP will be emitted. However, we can extrapolate the triplet concentration decay in PdTPBP; at early times this also follows a power law decay with slope approaching –0.95 (as in Figure 5b). From Figure 5b it is clear that the extrapolated emission intensity decreases from 3.7×10^8 to 4×10^6 (by 99%) during the time interval from 10 ps to 1 ns. This means that the triplet concentration on PdTPBP will decrease by approximately 99% due to TTA. We emphasize that this evaluation does not claim the exact number of triplets lost, but indicates the probable order of magnitude of quenching due to TTA on PdTPBP.

Now we turn our attention to triplet dynamics in the SY host as this is the crucial part of upconversion via triplet fusion process. This, too, we investigated by gated nanosecond spectroscopy and confirm that upconversion via triplet fusion is indeed responsible for energy upconversion in SY hosts (**Figure 7**). As can be inferred from Figure 7B, SY delayed fluorescence from 4% PdTPBP:SY films following selective excitation of the PdTPBP moieties at 1.96 eV is present even 10 µs after excitation indicating a very long lifetime of the emitting species. The only species with such a long lifetime at room temperature can be the triplet excited state in SY from which upconverted emission arises confirming that its cause is triplet fusion suggesting that this emission is not due to photon absorption.

In Figure 7A we have recorded DF intensity dependence at low excitation and high excitation fluencies i.e., when Equations (4) or (5) are valid respectively. Using Equation (4) we can show that in the first case the DF intensity should be proportional to the square of the excitation fluence (i.e., initial triplet concentration T_0):

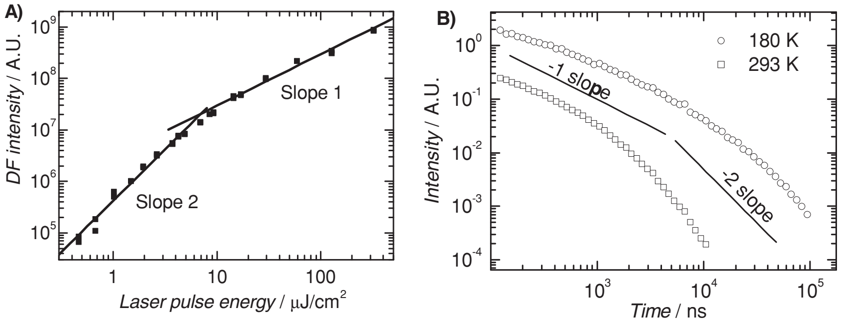

Figure 7. A) Dependence of SY delayed fluorescence (recorded 1 µs after excitation) from 4% PdTPBP:SY films on excitation energy (1.96 eV) at room temperature. B) SY delayed fluorescence decay from 4% PdTPBP:SY film excited with 1.96 eV laser at 180 K (circles) and at room temperature (squares, intensity offset for clarity).

$$DF \sim \int_0^\infty k_{tt}[T]^2 dt$$

$$= \int_0^\infty k_{tt}[T_0]^2 \exp(-2[k_r + k_{nr}]t)dt = \frac{k_{tt}[T]_0^2}{2(k_r + k_{nr})} \tag{6}$$

Using Equation (5) we show that in the second case the DF intensity follows linear proportionality on the excitation fluence (initial triplet concentration T_0):

$$DF \sim \int_0^\infty k_{tt}[T]^2 dt = \int_0^\infty k_{tt}\frac{[T_0]^2}{(1 + k_{tt}[T_0]t)^2} dt = \frac{k_{tt}[T]_0^2}{k_{tt}[T_0]} = [T_0] \tag{7}$$

As Equation 6 predicts, DF arising from triplet fusion indeed follows a quadratic dependence on the initial triplet concentration (or laser pulse energy) (Figure 7A). At higher excitation densities it starts to follow a linear relationship as then triplet fusion is dominant; this is in line with Equation (7) and with previous observations in other organic films where DF from triplet fusion is present.[39–41] This also has been observed previously in other upconversion via triplet fusion experiments.[43,44]

Further, from Equation (5) we can derive the delayed fluorescence dependence on time. If triplet fusion is the dominant process in the system then the delayed fluorescence intensity should be proportional to change of the triplet population over time:

$$DF \sim k_{tt}[T]^2 = k_{tt}[T_0]^2 \frac{1}{(1 + k_{tt}[T_0]t)^2} \tag{8}$$

At high intensities and moderately long times $k_{tt}[T_0]t >> 1$[39] leading to

$$DF \sim \frac{k_{tt}[T_0]^2}{(k_{tt}[T_0]t)^2} \sim t^{-2} \tag{9}$$

The decays in Figure 7B were recorded at >100 μJ/cm^2 per pulse, i.e., at excitation energy when triplet fusion is dominant hence Equations (5), (8) and (9) should be more suitable for the description of the process than Equations (3) or (4). In this case, DF vs time should decay with a power law having an exponent -2 if triplet migration is non-dispersive, i.e., k_{tt} is time-independent.[39–41] This is observed at later times for both temperatures in Figure 5B. In the initial time region, however, the decay follows slope ≈–1. Such decay dynamics have already been observed in other organic films, namely, polyfluorene[39,41] and NPB[40] and have been ascribed to dispersive migration of triplet population. This happens when triplets generated randomly in the density of states (DOS) relax towards the tail of the DOS, making k_{tt} time-dependent. In such circumstances Equation (2) and its solutions cannot be used to describe the process and more complicated theories need to be employed.[45–47] It has been shown numerous times that the process of a triplet population migrating in a dispersive manner cannot be cast into a simple analytical expression and this –1 slope assignment to dispersive migration is drawn from the entirety of evidence, namely, experimental results,[39–41] Monte-Carlo simulations[48,49] and theoretical solutions derived using limiting assumptions.[47] Also as observed in polyfluorene[41,39] and NPB films,[40] the turnover between the dispersive regime (slope –1) and non-dispersive described by Equation (4) (slope –2) takes place later at higher temperatures. The repercussions of dispersive migration on the efficiency of upconversion via triplet fusion are unclear at the moment and more investigation is underway on the evaluation of triplet fusion efficiency in hosts.

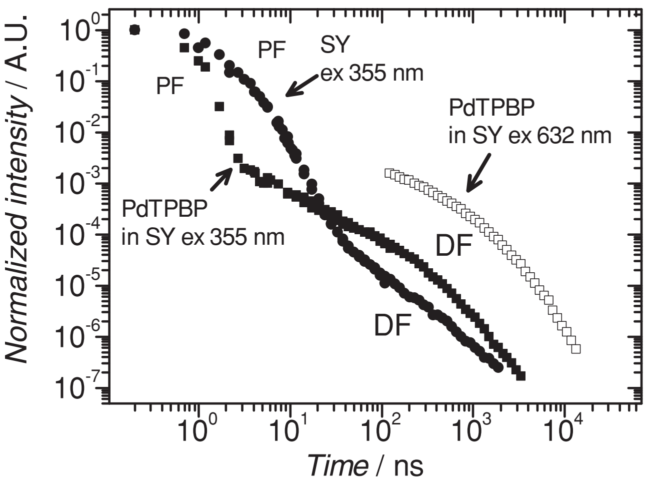

Figure 8. Decays of SY from 4% PdTPBP:SY excited at 355 nm (squares) and at 632 nm (open squares) and pure SY films excited at 355 nm (circles). The first cascade-like feature on the log-log scale is prompt fluorescence (PF), the second is delayed fluorescence (DF). From this type of data (when excited at 355 nm) and Equation (10) we evaluate the yield of delayed fluorescence (more details in text).

2.4. Efficiency Evaluation

From the luminescence decay curves (**Figure 8**) we can evaluate the yield of delayed fluorescence. Reports on efficiency evaluation of upconversion in soft materials in polymer matrices have already appeared.[50] Here we propose a different method and excite the 4% PdTPBP:SY blended film at 355 nm and estimate the ratio of delayed fluorescence to prompt fluorescence. Only SY absorbs significantly at 355 nm, as the dopant concentration is very small, confirmed from absorption spectra of pure and blended films. Singlet excitons from SY are transferred to the dopant singlet level with the yield ϕ_{SS}, and cross to the triplet manifold with an intersystem crossing yield ϕ_{ISC}. Finally excitons are transferred to SY triplet state with the yield ϕ_{TT}. A fraction of the delayed fluorescence in the blend film can arise from inherent SY delayed fluorescence which is not related to the dopant i.e., directly produced delayed fluorescence from intrinsic SY triplet fusion. We denote this inherent SY delayed fluorescence, ϕ_{SYT}, and this can be estimated from delayed fluorescence (DF) and prompt fluorescence (PF) decay ratios measured in pure SY films excited at 355 nm ($DF/PF_{pure} = \phi_{SYT}$) (Figure 8 plotted in black circle symbols). In the blend films, triplet excitons undergo fusion with a yield ϕ_{DF}. The DF/PF ratio of blend films depends on these parameters following;

$$\frac{DF}{PF}_{blend} = \frac{F_{inst}N_s\phi_f(\phi_{SS}\phi_{ISC}\phi_{TT}\phi_{DF} + \phi_{SYT})}{F_{inst}N_s\phi_f} \tag{10}$$

where F_{inst} is an instrumental function (optical collection), N_s is number of excited states, ϕ_f is SY fluorescence quantum yield. The equation can be simplified substantially. F_{inst} is the same for PF and DF as they are recorded during the same measurement, as is the initial number of excited states after pulsed excitation. All quenching mechanisms including intersystem crossing, non-radiative decay rate, and quenching due to exciton migration are accounted for in ϕ_f and are identical for both types of emission as they come from the same singlet state. Meanwhile, ϕ_{ISC} for PdTPBP is nearly 1.[15] We need to determine Y, which is the delayed fluorescence yield in blended films arising from triplet fusion via the dopant mechanism:

$$Y = \phi_{SS}\phi_{TT}\phi_{DF} \tag{11}$$

which can be found using the following expression:

$$Y = \frac{DF}{PF}_{blend} - \frac{DF}{PF}_{pure} = \phi_{SS}\phi_{TT}\phi_{DF} \tag{12}$$

After numerous repeated measurements, we estimated DF/PF_{pure} to be ≈20% of DF/PF_{blend} and evaluated Y in the 4% PdTPBP:SY film to be 0.06. Considering these films are not optimized and the sensitizer concentration is kept rather low, this value is promisingly high. If we assume ϕ_{DF} is 0.5 (maximum possible) then Y can also have a maximum of 0.5. From the integrated difference between pure and doped film normalized PF areas, we estimate a lower limit of ϕ_{SS} to be ≈0.5. For the doped film we measured PF decay to be ≈0.3 ns which is very near the resolution limit of our system. Very likely the convolution of our system jitter and laser pulse length with the decay of the blended film leads to an over estimate of the amount of PF in the blend films. Note, however, that this yield is not important for applications, as the dopant will be excited directly. More important to us is the triplet-dopant-to-host transfer yield (ϕ_{TT}). Using our values in Equation (12) reveals that ϕ_{TT} should be ≈0.06/0.5/0.5 = 0.24 or even smaller. We propose that this huge loss in ϕ_{TT} arises from aggregation of PdTPBP molecules and subsequent triplet-triplet annihilation in these dopant aggregates. The ≈76% loss of triplets when transferred from PdTPBP to SY also agrees well with our estimations of triplet loss due to triplet annihilation on PdTPBP aggregates above (99%) using phosphorescence decay of PdTPBP from PdTPBP:SY films. The agreement is good considering that the evaluation methods of aggregate quenching are substantially different.

3. Conclusions

Upconversion via triplet fusion in a solid state has already been investigated previously. Upconversion in polymer hosts doped with porphyrin sensitizers has been reported, namely in poly-9,9-bis(2-exyl-hexyl)fluorene[51] and poly-spirobifluoreneanthracene.[52] However, these hosts have triplet levels that are too high (≈2.2 eV) to host deep red, near infrared sensitizers (SY triplet level is 1.5 eV). Researchers also have observed upconversion in inert polymer matrices. For example, Castellano et al. doped palladium metal complexes and DPA or rubrene into a copolymer of ethylene-oxide and epichlorohydrin.[28,53] Similarly, upconversion in cellulose acetate and polymethylmethacrylate has been observed.[29,54] This could reduce the efficiency of TF due to the larger separation between triplet excitons and very poor triplet mobility between active sites resulting in lower triplet densities. Recently, more exotic approaches have been reported, for example, nanocrystalline ZrO_2 film co-sensitized with metal-phorphyrin derivative and DPA.[55] Also commercially available polyurethane precursors (Clear Flex 50) in combination with palladium porphyrin and DPA have been reported to give very high upconversion yields.[50] However, this work is still in its infancy and alternatives are desirable. In this paper we choose a polymer as a host material, but with much lower triplet level than previously reported, and palladium phorphyrin sensitizer. Indeed, if high upconversion efficiency could be achieved in a polymer host, it would be easy to transfer it to device fabrication drawing on previous experience of spincoating and slot-coating of OLED devices. Hence, we analyse triplet dynamics in this system in details in femtosecond, picosecond and nanosecond time domains. The intersystem crossing rate constant of PdTPBP was determined to be 1.8×10^{11} s^{-1}. It was shown that the rate constant for triplet transfer from PdTPBP to SY is 10^9 s^{-1}. The latter value is much slower than that predicted from energy transfer alone, which has been established to occur at a rate of the order of 10^{11} s^{-1}.[30,36,37] Given that Dexter energy transfer is a short-range process, PdTPBP triplet excitons are first required to migrate to an interface between PdTPBP and SY before energy transfer can occur. It has been shown that during this migration in PdTPBP aggregates, 76–99% triplets in PdTPBP are lost due to triplet annihilation in PdTPBP. Indeed, we evaluated the upconversion via triplet fusion efficiency in the 4% PdTPBP:SY film to be 6%. We then show that the main upconversion efficiency loss mechanism in 4% PdTPBP:SY films is due to exciton recombination in sensitizer aggregate domains, the existence of which is proven by steady state absorption spectra. All experimental evidence points to the possible way of improving the efficiency: the size of the PdTPBP domains needs to be reduced, thus reducing the number of excitons which recombine before undergoing energy transfer to the host. This could be done by introducing bulkier moieties to the sensitizer or by optimizing sensitizer concentration and solvents used for spincoating in combination with annealing and similar temperature treatments. This could possibly lead to higher upconversion via triplet fusion efficiencies and non-coherent upconversion via triplet fusion in SY films. Triplet dynamics in the host SY have also been investigated in this paper and it was proven that triplet fusion takes place in SY host and that, at early times, migration of triplets in SY host is of a dispersive manner and later turns into classical non-dispersive migration. The influence of dispersive migration on the efficiency of the process of upconversion via triplet fusion in a host needs to be investigated more thoroughly. All in all, here we have developed a clear picture of the physical processes that can affect the up-conversion efficiency in films, and loss of triplet excitons prior to energy transfer to the host material is one such mechanism.

4. Experimental Section

Details of Synthesis and Characterization of PdTPBP: The ^{1}H and ^{13}C NMR spectra were recorded on a Varian 700 MHz instrument. Chemical shifts (δ) are in ppm, referenced to residual protio-solvent resonances, and coupling constants are in Hertz. The MALDI mass spectrum was recorded with a Bruker Daltonik Autoflex II ToF spectrometer and the accurate mass by ASAP, using a Waters LCT Premier XE mass spectrometer.

A solution of 5,10,15,20-tetraphenyl-tetrabenzoporphyrin (50 mg, 0.061 mmol) in THF (40 mL) was purged with N_2 for 30 min. $Pd(MeCN)_2Cl_2$ (31 mg, 0.12 mmol) in THF (10 mL) was added under a positive pressure of N_2 and the mixture refluxed in the absence of light for 3 h, after which triethylamine (50 µL) was added and the mixture refluxed for a further 17 h. After cooling to room temperature the reaction mixture was filtered through a plug of Celite, the product washed through with additional THF and the solvent removed under reduced pressure. Purification was achieved by flash column chromatography (silica; gradient elution from hexane to 80% hexane/20% ethyl acetate) to give the desired product as a green solid (41 mg, 73%). The structure of PdTPBP and the atom numbering scheme used in the assignment of 1H NMR is shown in the Supporting Information.

^{1}H NMR ($CDCl_3$, 700 MHz) $\delta_H = 8.27$ (8H, dd, $^3J = 7.5$, $^4J = 1.5$, $H^{2''}$), 7.92 (4H, tt, $^3J = 7.5$, $^4J = 1.5$, $H^{4''}$), 7.85 (8H, dd, $^3J = 7.5$, $^4J = 1.5$, $H^{3''}$), 7.21 (8H, dd, $^3J = 6.5$, $^4J = 3.0$, $H^{2'}$), 7.12 (8H, dd, $^3J = 6.5$, $^4J = 3.0$, $H^{1'}$). ^{13}C NMR ($CDCl_3$, 176 MHz) $\delta_C = 142.4$ (4C, $C^{1''}$), 139.1 (8C, C^1), 138.5 (8C, C^2), 134.5 (8C, $C^{2''}$), 129.7 (8C, $C^{3''}$), 129.6 (4C, $C^{4''}$) 125.8 (8C, $C^{2'}$), 124.4 (8C, $C^{1'}$), 118.6 (4C, C^5). MS (MALDI, dithranol matrix): m/z = 917.4 $[M]^+$. HRMS ($ASAP^+$): $m/z = 915.2058$ for $[M + H]^+$; calculated for $^{102}PdC_{60}H_{37}N_4$, 915.2074. TLC (silica) $R_f = 0.37$ in hexane/ethyl acetate (4:1). Mp > 250 °C.

Sample Preparation and Photophysical Measurements: Super yellow polymer (SY) and PdTPBP were dissolved in toluene stirring overnight and heated at 80 °C for 30 min on a hotplate prior to mixing solutions together to get 4% PdTPBP mass to mass ratio in SY with final 3 mg/ml concentration of SY. Blend solutions were heated at 80 °C for 5 min. before drop casting onto preheated (80 °C) sapphire substrates; samples were left on the hotplate for ca. 15 min to allow complete solvent evaporation. Similar procedures were used for PdTPBP doped in zeonex with the difference that the mass to mass ratio was 0.1%. Samples were placed into displex cryostat (vacuumed with turbomolecular pump) for both room temperature and low temperature measurements. Nanosecond gated luminescence and lifetime measurements were made using a system consisting of a 1.96 eV dye laser pumped with high energy pulsed YAG laser emitting at 2.33 eV (EKSPLA). Samples were excited at 45° angle to the substrate plane. Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) with sub nanosecond resolution. Decay measurements were performed by logarithmically increasing gate and delay times; more details can be found elsewhere.[41]

Ultrafast transient absorption spectroscopy was performed using a conventional femtosecond non co-linear pump-probe setup. Laser pulses (180 fs, 4 µJ, 100 kHz repetition rate) at 780 nm were generated using a Coherent Mira900-f Ti:Sapphire femtosecond oscillator in conjunction with a Coherent RegA 9000 laser amplifier. The amplifier output was used to drive a Coherent 9400-OPA, with the single wavelength (1.72-2.79 eV) and white-light supercontinuum (1.24–2.64 eV) OPA outputs used to generate pump and probe respectively. The variable delay between pump and probe pulses was controlled by means of a motorised linear translation stage (Newport). A variable λ/4 waveplate was introduced to the pump path and used to orient the pump at 54.7° (magic angle) with respect to the probe to ensure the transient data obtained was independent of polarization.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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