Electronic Supplementary Information

Photon-upconverter for blue organic light-emitting diodes: a low-cost, sky-blue example

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Section 1: DPBF singlet decay

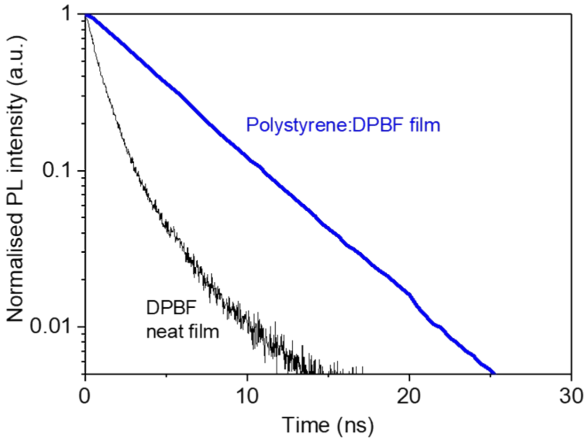

Fig. S1 TCSPC measurement of a neat DPBF thin film and a blend polystyrene:DPBF thin film.

For spin-coated DPBF neat films, photoluminescence (PL) spectrum and PL peak decay kinetics by time-correlated single-photon counting (TCSPC) are shown in Fig. S1. Its sky-blue peak at 490 nm shows singlet exciton decay characteristics, with a lifetime of ~2 ns in neat film, and ~6 ns in a blended film with inert polymer polystyrene. The fast quenching of singlet lifetime in a neat film can be considered as an indication of singlet fission being present. Singlet fission is reduced in the blend film, as DPBF molecules are dispersed in the polymer, and the extent of interchromophore coupling necessary for singlet fission is then weakened. Although triplet fusion is also a bimolecular event, we can only speculate from such general data that its need for aggregation or intermolecular interaction is lower than its fission counterpart, although this has not been and cannot be conclusively validated based on such simple observations.[1–3]

Section 2: Optically-excited TTA-UC in DPBF

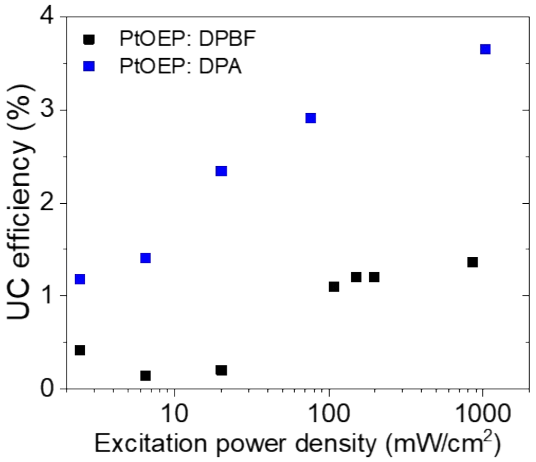

Fig. S2. Optically excited TTA-UC systems – comparison between DPBF and well-known DPA upconverter, both sensitized by the same PtOEP, under similar conditions.

These measurements were performed to illustrate DPBF’s TTA-upconversion ability compared with a well-known system, the PtOEP:DPA system. Performed under similar conditions, under excitation by a CW laser of 532 nm, and solution mixture prepared in nitrogen-filled glovebox in anhydrous (not de-oxygenated) DMF solvents. Under such ***un-optimised*** conditions, we observe that DPBF demonstrates an upconversion efficiency of ~1.2-1.4% above 100 mW/cm^2, and DPA has an upconversion efficiency of >3% above 100 mW/cm^2, based on a maximum theoretical upconversion efficiency of 50% (due to the two-for-one phenomenon of TTA-UC).

Section 3: Hole-only device

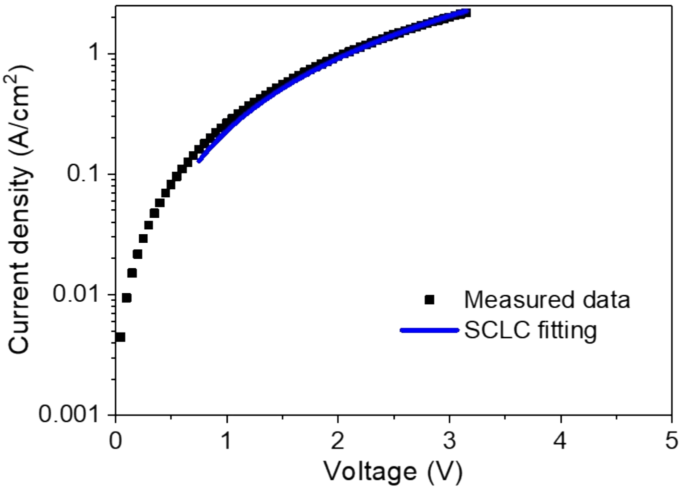

Fig. S3. Current-voltage characteristics of a DPBF hole-only device, fitted with the SCLC model.

Single-carrier (hole-only) devices of structure ITO/PEDOT:PSS or MoO_x/DPBF (spin-coated)/MoO_x/Au) are fabricated. Injecting holes from either the PEDOT:PSS or the MoO_3/Au side generated nearly identical and symmetrical current-voltage (*J*-*V*) curves. To extract hole mobilities, the *J*-*V* curves are fitted with a space charge limited current (SCLC) model, extensively explored by Lampert and Mark. Fig. S3 shows such a *J*-*V* curve with fitting over its SCLC regime, yielding a hole mobility of 0.083 cm^2 V^{-1} s^{-1}. Processing conditions are likely to be crucial, although it was not investigated in detail. Solvents used for solution-deposition would greatly affect the intermolecular interaction and crystallinity during film formation/drying. Annealing is most likely to be critical. These were not investigated in detail. The hole-only devices here were prepared with unannealed DPBF spun from chlorobenzene solution, to give ~350 nm thick films as confirmed by surface profile measurements.

Section 4: Methods

Materials

All materials and solvents were purchased and used as received. 1,3-Diphenylisobenzofuran (DPBF), platinum octaethylporphyrin (PtOEP) were purchased from Sigma Aldrich. Most other materials mentioned below have been purchased from Sigma Aldrich unless otherwise stated.

Solution-phase TTA-UC experiments

PtOEP was used as a triplet sensitizer and DPBF as a triplet acceptor. All materials were used as purchased without any further purification. Anhydrous dimethylformamide (DMF) from Sigma Aldrich was used as a solvent. The solution-based sample was prepared in a nitrogen-filled glovebox. Firstly, PtOEP and DPBF were weighed and dissolved in DMF to obtain the stock solutions. Then, the fresh samples for measurement were prepared from the stock solutions with the concentrations of PtOEP being 25 μM and that of DPBF being 2.4 to 9.0 mM. For measurement, the as-prepared solution was placed in quartz cuvette of path length 10 mm closed with a stopcock.

The TTA-UC spectra were obtained by using an absolute quantum yield measurement setup, including an integrating sphere with a diameter of 12 cm, a continuous wave (CW) laser with a wavelength of 532 nm and a high-performance spectrometer (Ocean Insight). The CW laser was used as excitation source for TTA-UC measurement and the power density could be controlled by using neutral density filters. In the TTA-UC measurement, the cuvette was placed in the integrating sphere and excited by the laser source at different power densities. The exact power densities of the laser excitation source were measured using a Gentec-eo power density meter.

Thin films for steady-state measurements

Films were spincoated on quartz substrates for PL and TCSPC measurements. The films were either placed under vacuum or immersed in nitrogen. Samples were typically excited optically with a 407 nm or 470 nm pulsed laser, with pulse width <200 ps and a repetition rate of 2.5 MHz. PL emission was captured by a single-photon avalanche photodiode. Instrument response function lifetime was ~200 ps. PL response was collected using a grating monochromater and spectrograph (Acton SpectroPro 2500i).

FuLED fabrication and characterisation

ITO-patterned glass substrates were cleaned by sonication in acetone and IPA for 10 min respectively. They were then oxygen plasma-etched at 250 W for 10 min. PEDOT:PSS (Clevios PV P AI4083) layer was first spincoated through a 0.45 μm GXF/GHP filter to yield a 20 – 30 nm film, and subsequently annealed under nitrogen at 150-200 °C for 15-20 min. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl)diphenylamine)] (TFB, Lumtec) was next deposited by spincoating through a PTFE filter in the glovebox to achieve a thickness of 200 nm, followed by thermal annealing of the films at >180 °C for 20 min. Polyvinylcarbazole (PVK):DPBF blend films, with DPBF doped 20 wt%, were filtered through PTFE filter and spincoated at 2000 rpm for 45 sec in a glovebox, followed by annealing at 90 °C, forming a ~20 nm layer. Bathophenanthroline (BPhen) solution was also filtered through PTFE filter and spincoated on top, for electron-transporting layer, and annealed at 60 °C. Finally, LiF (~1 nm, 0.05 Å/s) and Al (100 nm, 0.5 – 3 Å/s) were deposited by thermal evaporation under vacuum (3×10^{-6} mbar) over a shadow mask. Electrical contacts were lastly affixed to the devices.

Electroluminescence (EL) spectra were collected using an optical fibre attached to the Labsphere CDS-610 spectrometer. A silicon photodiode with an active area of 100 mm^2 collected EL photons from the LED device. A Keithley 2400 source meter supplied the voltage input, and a Keithley 2000 source meter measured the output of the photodiode. Current-voltage-luminance characterisation was recorded as such.

Evolution of EL spectra were captured with an electrically-gated intensified CCD (ICCD) camera (Andor iStar DH740 CCI-010) and a calibrated grating spectrometer (Andor SR303i). The devices were electrically excited by a function generator using 1 kHz square voltage (current) pulses with a pulse width of 0.5 ms for the on-cycles (forward bias). When pulse length needed to be varied, a range of 1 – 500 μs was used. Up to 10 V was applied to the devices under measurement. The off-cycles of the device operation were provided by a reverse bias of –4 V to eliminate charge accumulation effects.

Hole-only device fabrication and characterisation

On clean and oxygen plasma-treated ITO substrates, PEDOT:PSS was first deposited as described above under FuLED fabrication. Alternatively, MoO_3 (20 nm) was deposited instead of PEDOT:PSS, by vacuum sublimation under a base pressure of 3×10^{-6} mbar. DPBF (~100 mg/mL in chlorobenzene) was then spincoated on top of the hole-transport layer. Finally MoO_3 (10 – 25 nm) and Au (80 nm) were sublimed under vacuum (3×10^{-6} mbar) over a shadow mask. Current-voltage characteristics were recorded with a Keithley 2636A source measure unit. Mobility was then analysed according to the space-charge limited current (SCLC) model. Film thicknesses were measured by AFM (Nanoscope IIIa) and thickness profile meter (Dektec).

Section 5: Calculations of $\eta_{\text{TTA-UC}}$ and $\Phi_{\text{TTA-UC}}$ in FuLEDs [2]

The intrinsic efficiency of TTA-UC can be seen as $\eta_{\text{TTA-UC}}$ = 2 x (number of singlets generated by TTA-UC) / (number of triplets entering the TTA-UC system):

$$\eta_{TTA-UC} = \frac{2 \times f_{delayed} \times IQE_{EL} \div PLQE}{f_{excitons} \times f_{triplets}} = \frac{2 \times f_{delayed} \times EQE_{EL}}{f_{excitons} \times f_{triplets} \times f_{outcoupling} \times PLQE}$$

Where IQE_{EL} and EQE_{EL} are the internal and external quantum efficiencies of the FuLED, $f_{delayed}$ is the percentage of the delayed EL in the total EL, $f_{excitons}$ is the formation probability of excitons from externally injected charges, $f_{triplets}$ is the fraction of triplet excitons in the initial exciton population formed by charge injection, $f_{outcoupling}$ is the optical outcoupling efficiency of the LED, and PLQE is the photoluminescence quantum yield of DPBF (0.85). $f_{excitons}$ is assumed to be 1 for the most conservative estimation. $f_{triplets}$ is assumed to be 0.75 according to spin statistics. $f_{outcoupling}$ is assumed to be 0.2. When using the maximum EQE of 6.5% obtained in this work, this gives the $\eta_{\text{TTA-UC}}$ as 44.8%.

The triplet-to-photon quantum yield, or the TTA-UC quantum yield, $\Phi_{\text{TTA-UC}}$, refers to the number of TTA-generated photons being emitted per every triplet exciton entering the TTA-UC system. This can be seen as:

$$\Phi_{TTA-UC} = \frac{f_{delayed} \times IQE_{EL}}{f_{excitons} \times f_{triplets}} = \frac{f_{delayed} \times EQE_{EL}}{f_{excitons} \times f_{triplets} \times f_{outcoupling}}$$

Using the maximum EQE of 6.5% obtained in this work, $\Phi_{\text{TTA-UC}}$ would be 19.0%.

Section 6: Difference in PL and EL spectra of DPBF

There are several possibilities for why EL and PL of organic/polymer blends differ, and why there is a more prominent shoulder in the EL compared to PL spectrum – we highlight here a few mostly likely causes:

1) Slight microcavity effect in OLED: This refers to the optical propagation of photons within the OLED device stack (i.e. considering the reflective electrode, and multiple layers of materials). This is absent, or much less significant, in a bare blend-film (PL in Fig 2a). The weak microcavity effect could lead to difference in overall emission profile/characteristics (due to different photons having different optical lengths) in the EL spectrum (Fig 3a).
2) Shifting of recombination zone in OLED towards DPBF/BPhen interface: In an ideal device, the holes and electrons injected at each electrode should travel towards the emissive layer (charge balance), and excitons should form at and recombine within the emissive layer. But we see in our findings that DPBF seems to have a good hole mobility, prompting our suggestion that the recombination zone does not fall exactly in the middle of our thin (20-30nm) emissive layer, i.e. slight charge imbalance. Instead, the recombination zone is likely to move towards the electron-transport layer (i.e. towards BPhen). This could lead to potential excitons formed at the DPBF/BPhen interface, which coincides with the greener shoulder around 520-530nm. This can also be likened to an (unintended) exciplex emission. This increased interfacial emission implies charge imbalance, further corroborating that our device structure is still not fully optimised, and that EQE rolls off more at higher current densities. Meanwhile this would also imply the DPBF FuLED could achieve higher efficiencies.
3) Film processed from different solvent/thickness: We have kept the dopant concentration of DPBF in PVK constant at 20% in both the PL and EL measurements. But in order to measure PL more easily, we processed the mixture in a lower boiling solvent tetrahydrofuran, and at higher overall concentration, to result in a thicker film of >100nm for PL. (Note in EL/OLED, the emissive layer is only 20nm thin, and processed from DMF). We may speculate that the more pronounced redder shoulder implies better pi-pi packing/aggregation when the film is processed from DMF.

References

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