The performance of conjugated polymers as emitters for triplet–triplet annihilation upconversion†

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A series of poly(phenylene–ethynylene) copolymers with various aryl spacer units were synthesized for use as emitters in triplet–triplet annihilation upconversion. The upconversion performance of these conjugated polymers was compared to that of well-known poly(phenylene–vinylene) polymers, MEH-PPV and super yellow, in chloroform solution. The copolymer containing anthracene units outperformed both reference polymers recording a maximum upconversion quantum yield of 0.18%.

Introduction

Triplet–triplet annihilation upconversion (TTA-UC), also known as triplet fusion upconversion, is a photochemical process by which two lower energy photons can be combined to produce one photon of higher energy.1 It sees use in raising the efficiency of solar cells above their thermodynamic limit (the Shockley–Queisser limit).2,3

Two chromophores are required in a typical TTA-UC system—a triplet sensitizer and an annihilator/emitter.1 The triplet sensitizer absorbs a photon promoting it to its singlet excited state (Fig. 1a). Intersystem crossing (ISC) leads to the formation of the triplet excited state on the sensitizer. This triplet exciton can then be transferred to an emitter molecule via triplet energy transfer (TET). As the triplet exciton population of emitters builds, two triplet excitons can combine leading to triplet–triplet annihilation (TTA) generating a higher energy singlet exciton. This singlet exciton then undergoes radiative decay releasing a photon that is higher in energy than the photon absorbed by the sensitizer.

Transition metal complexes are most commonly used as triplet sensitizers but metal chalcogenide quantum dots have also been used.4,5 As for the emitter component, polycyclic aromatic hydrocarbon molecules have been widely investigated.6–9 Much less well-established is the use of conjugated polymers as emitters in TTA-UC.10–14 It was shown in theoretical models that the extended conjugation of these materials leads to improved triplet exciton diffusion which may assist in TTA-UC performance.15 Measurements of TTA-UC systems containing conjugated polymers showed some promise but accurate comparison of TTA-UC efficiency has not been reported.14,16 In this study, the TTA-UC...
performance of several conjugated polymers in solution was investigated and compared (Fig. 1b).

There are some important parameters to consider when measuring TTA-UC performance.\textsuperscript{17} The TTA-UC efficiency is measured by the upconversion quantum yield ($\Phi_{\text{UC}}$), which is a product of all the quantum yields for photochemical processes involved, given by the equation:

$$\Phi_{\text{UC}} = \Phi_{\text{ISC}} \Phi_{\text{TET}} \Phi_{\text{TTA}} \Phi_{\text{PL}}$$  \hspace{1cm} (1)

where $\Phi_{\text{ISC}}$ is the intersystem crossing quantum yield, $\Phi_{\text{TET}}$ is the triplet energy transfer quantum yield, $\Phi_{\text{TTA}}$ is the TTA quantum yield, and $\Phi_{\text{PL}}$ is the photoluminescent quantum yield.\textsuperscript{16} $\Phi_{\text{TTA}}$ can be further separated into the contact triplet pair formation efficiency and the factor $f$,\textsuperscript{16} which is a measure of the probability of generating the singlet excited state after TTA, since singlet, triplet and quintet states are all possible outcomes. This factor may differ significantly between different emitter molecules.\textsuperscript{18–20}

In measuring $\Phi_{\text{UC}}$, a relative measurement is typically preferred due to its simplicity.\textsuperscript{21} This can be done by comparing the integrated photoluminescence intensity of a standard fluorescent dye with a known $\Phi_{\text{PL}}$ and that of the upconversion dye pair, eqn (2):

$$\Phi_{\text{UC}} = \frac{A_{\text{std}}}{A_{\text{Unk}}} \left( \frac{I_{\text{Unk}}}{I_{\text{std}}} \right) \left( \frac{\eta_{\text{Unk}}}{\eta_{\text{std}}} \right)^2$$  \hspace{1cm} (2)

where $A$ is the absorbance, $I$ is the integrated photoluminescence intensity, $\eta$ is the refractive index of the medium and $\Phi_{\text{std}}$ is the $\Phi_{\text{PL}}$ of the standard. The $\Phi_{\text{UC}}$ value of upconversion systems can also be determined using absolute quantum yield method.\textsuperscript{22} Previous studies on conjugated polymers in TTA-UC did not report on the $\Phi_{\text{UC}}$ value determined using either absolute or relative method.\textsuperscript{10–14}

Herein, the $\Phi_{\text{UC}}$ of solutions containing commercially available poly(phenylene–vinylene), MEH-PPV and super yellow, were measured using an absolute quantum yield method with mesotetraphenyl-tetrabenzo porphine palladium complex (PdTPPBP) as the triplet sensitizer. We then compare the performance of MEH-PPV and super yellow to a series of poly(phenylene–ethynylene) copolymers. The TTA-UC samples were in a similar concentration of polymer in chloroform using anthracene as a reference with excitation at 350 nm.

### Results and discussion

A series of copolymers based on poly(phenylene–ethynylene) (PPE) was devised bearing dioctylfluorene sidechains to increase polymer solubility and to reduce molecular interactions that increase the rate of non-radiative decay (Fig. 1). It is well-known that PPEs with alkyl sidechains can show strong molecular association leading to low photoluminescence quantum yield.\textsuperscript{21} The aryl comonomer unit was varied to fine tune the photophysical properties of the polymer backbone.

The bis-ethyne monomer 4 was synthesized by Suzuki coupling followed by treatment with TBAF to remove the TMS protecting groups in 74% yield (Fig. S2, ESI†). The single crystal structure of monomer 4 was obtained by slow evaporation from a chloroform solution. The structure showed a slip packed, with a symmetrical kink in of one of the octyl chains on each of the fluorene units caused by close packing (for further details see Table S1, ESI†). The para-aryl dibromide monomers 5a–d were either commercially available or synthesized using literature methods (see ESI† for details).

The polymers were synthesized using Sonogashira polycondensation between monomer 4 and dibromide monomers 5a–d, with reaction yields varying between 41–66% (Table S2, ESI†). The molecular weight of the polymers was found to be fairly low (<15 000 g mol\textsuperscript{-1} (Table 1, see ESI† Fig. S7 for GPC traces).

| Table 1  | Properties of PPE copolymers 1a–d |
|----------|----------------------------------|
|          | $M_n$ (g mol\textsuperscript{-1}) | $D$ | DP\textsuperscript{a} | Abs $\lambda_{\text{max}}$ (nm) | PL $\lambda_{\text{max}}$ (nm) | $\Phi_{\text{PL}}$ \textsuperscript{b} (%) |
| 1a       | 11 600                           | 2.0 | 11 | 321 | 533 | 49.5 ± 0.2 |
| 1b       | 5310                             | 1.6 | 7  | 319 | 462 | 97.8 ± 2.1 |
| 1c       | 7070                             | 1.6 | 9  | 320 | 450 | 74.5 ± 1.5 |
| 1d       | 5910                             | 1.9 | 6  | 323 | 445 | 93.8 ± 2.2 |

\textsuperscript{a} DP = degree of polymerization.  \textsuperscript{b} Solution $\Phi_{\text{PL}}$ measured at 10 μg mL\textsuperscript{-1} concentration of polymer in chloroform using anthracene as a reference with excitation at 350 nm.

Attempts to increase these values proved to be unsuccessful. Neither longer reaction times nor higher temperatures had any effect on the molecular weight. Similarly, no change was noticed when the corresponding para-aryl diiodides were used in place of the para-aryl dibromides 5. When using Pd(dppf)Cl\textsubscript{2} as the catalyst, a slightly higher molecular weight range was obtained, however the polymers produced were weakly emissive. Similar PPEs reported in prior literature also exhibited low molecular weights with Sonogashira polycondensations.\textsuperscript{24–26} Higher molecular weights in homopolymers could be obtained by alkyne metathesis,\textsuperscript{27} however this method is difficult to implement for construction of copolymers. Concerning the polymer properties for TTA-UC, it should be noted that as little as 5 repeat units have been shown to be sufficient for similar photophysical properties as the corresponding PPE.\textsuperscript{24}

The photoluminescence spectrum of the copolymers showed some variation in the peak emission with the most significant difference for anthracene copolymer 1a. The extended π system of the anthracene in 1a led to the most red-shifted UV-Vis absorption edge and photoluminescence (PL) peak maxima in the series (Fig. 2). All copolymers have an absorption maximum at ~320 nm which can be attributed to the fluorene sidechains.\textsuperscript{28} Copolymer 1a also showed vibronic features in its absorption and PL spectra reminiscent of the anthracene building block. The $\Phi_{\text{PL}}$ of the polymers ranged from 50% to 100% (Table 1), with the anthracene derivative 1a being the least emissive and the naphthalene derivative 1b being the most emissive. The most likely reason for the $\Phi_{\text{PL}}$ variations is the positioning of the fluorene sidechains and their effect on polymer–polymer interactions. Some insights are discussed in the DFT calculations section below. These PLQY values are reminiscent of many PPE copolymers, with solution $\Phi_{\text{PL}}$ values reminiscent of many PPE copolymers.
maximum for 1a was close to that of the conventional photoluminescence excited state energy to interact with the PdTPTBP sensitizer. The upconverted emission intensity was optimized and found to occur using a polymer concentration of 0.25 mg mL\(^{-1}\) with a 7.5 \(\mu\)M concentration of PdTPTBP. Surprisingly, none of the other PPE derivatives showed any upconversion emission under the same conditions. In fact, the polymers 1b–d failed to quench the phosphorescence of PdTPTBP at 800 nm (Fig. 3). This is a clear indication that only 1a has appropriate triplet excited state energy to interact with the PdTPTBP sensitizer.

The upconverted emission maximum for the sample containing 1a was close to that of the conventional photoluminescence maximum for 1a at 540 nm but the emission profiles were rather different especially with the 600 nm banc pass filter used on the upconverted emission measurement (Fig. S15, ESI†).

These copolymers were then compared to commercially available PPV emitters – MEH-PPV and super yellow – whose \(\Phi_{\text{UC}}\) was determined via an integrating sphere method under nitrogen atmosphere to be 0.039% and 0.029% respectively. These values were determined in chloroform solution with an excitation intensity of 985 mW cm\(^{-2}\) at 632 nm, with an optimized polymer concentration of 0.5 mg mL\(^{-1}\) and PdTPTBP at 7.5 \(\mu\)M. Despite the higher \(\Phi_{\text{PL}}\) of super yellow at 69% compared to 27% for MEH-PPV, its \(\Phi_{\text{UC}}\) is lower than MEH-PPV.\(^{30,31}\) The lower upconversion intensity of super yellow and its substantially higher cost compared to MEH-PPV, makes MEH-PPV preferable as an upconversion standard. These commercial polymers serve as adequate standards, with a large degree of spectral overlap due to their broad photoluminescent emission in the same region displayed by the PPE copolymers.

The \(\Phi_{\text{UC}}\) values were measured as a function of the excitation intensity for 1a and MEH-PPV. A maximum \(\Phi_{\text{UC}}\) value of 0.18% was reached at 8910 mW cm\(^{-2}\) (Fig. 4). The \(\Phi_{\text{UC}}\) of MEH-PPV reached a maximum value of 0.065% at 10 500 mW cm\(^{-2}\). These values were also measured relative to super yellow PPV and found to have little to no relative error (Table S3, ESI†). Although these are low values of \(\Phi_{\text{UC}}\) compared to the best solution TTA-UC systems,\(^{32}\) this work showed PPE materials are possible emitters and performed significantly better than both MEH-PPV and super yellow.

To gain insight into the effect of various aryl monomer building blocks on the properties of the polymers, density functional theory (DFT) calculations were performed (Fig. 5 and 6). A semi-empirical method (PM6) was used to optimize the geometry of these polymers, then the TD-DFT was performed with B3LYP/6-311G(d,p) to obtain the singlet and triplet excited state energies. As mentioned previously, the difference in the \(\Phi_{\text{PL}}\) values (Table 1) could be related to the positioning of the fluorene sidechains. For the naphthalene and fluorene-based copolymers 1b and 1d, the sidechains of the optimized structures are directed inwards towards the arene units (Fig. 5). This is expected to reduce polymer–polymer backbone interactions leading to higher \(\Phi_{\text{PL}}\). For 1a and phenylene-based 1c,
the fluorene sidechains occupied the same plane, leaving the polymer backbone more exposed.

The electron distributions for the HOMO and LUMO of all polymers showed a high level of overlap (Fig. 5). Additionally, for the anthracene polymer, more of the electron distribution was found on the anthracene unit itself than for the other polymers, which mainly reside on the conjugated polymer backbone. This may explain the retained vibronic emission features seen in anthracene-based polymer 1a (Fig. 2).

The calculated singlet ($S_1$) and triplet ($T_1$) energies are shown in Fig. 6. These values are similar to a previous theoretical study on the energy levels of PPEs by Kohler and Beljonne, where $T_1$ of 1.51, 2.40 and 2.25 eV were found for the anthracene, phenylene and dioctylfluorene-based polymers respectively.\(^{14}\) The $T_1$ values of 1a and MEH-PPV, at 1.43 eV and 1.30 eV\(^{34}\) respectively, were lower than $T_1$ of the triplet sensitizer PdTPTBP.\(^{35}\) This indicated that energetically favourable triplet energy transfer from the sensitizer was possible for 1a and MEH-PPV. This agreed with observations in the phosphorescence quenching and TTA-UC emission measurements.

Although alternative triplet sensitizers could theoretically produce upconversion with copolymers 1b–d, no single sensitizer can work with all polymers in this study given the energy level requirements for TTA-UC. Instead, many of the polymers could be excited directly at sufficiently high excitation energies in preference to a sensitizer, resulting in down-converted emission. As the primary aim of this study was to assess the performance of conjugated polymers as emitters for upconversion and MEH-PPV/PdTPTBP was the reference system, only PdTPTBP was used.

### Conclusions

In summary, a series of PPE copolymers with a variety of aryl spacer units were synthesized and tested as emitters for TTA upconversion. Commercially available conjugated polymers, MEH-PPV and super yellow PPV, were used as references for $\Phi_{\text{UC}}$ measurements after their $\Phi_{\text{UC}}$ values were determined by absolute quantum yield method. The anthracene-based polymer 1a outperformed both references achieving maximum $\Phi_{\text{UC}}$ of 0.18% with 632 nm excitation and 8910 mW cm\(^{-2}\) intensity. Other copolymers in the series did not quench the phosphorescence of the sensitizer and therefore showed no upconverted emission. DFT calculations indicated only 1a has the appropriate triplet energy for triplet energy transfer from the PdTPTBP sensitizer. We are in the process of exploring the TTA-UC performance of a wider range of conjugated polymers to further assess their viability in photon upconversion applications.

### Abbreviations

| Abbreviation | Description |
|--------------|-------------|
| TTA          | Triplet–triplet annihilation |
| UC           | Upconversion |
| PPV          | Poly(phenylene–vinylene) |
| PPE          | Poly(phenylene–ethynylene) |
| DP           | Degree of polymerization |
| UV-Vis       | Ultraviolet-visible |
| PL           | Photoluminescence |
| PdTPTBP      | Palladium(II) meso-tetraphenyltetrabenzoporphyrin |
| DFT          | Density functional theory |
| TD           | Time dependent |
| HOMO         | Highest occupied molecular orbital |
| LUMO         | Lowest occupied molecular orbital |

### Conflicts of interest

There are no conflicts to declare.
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