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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

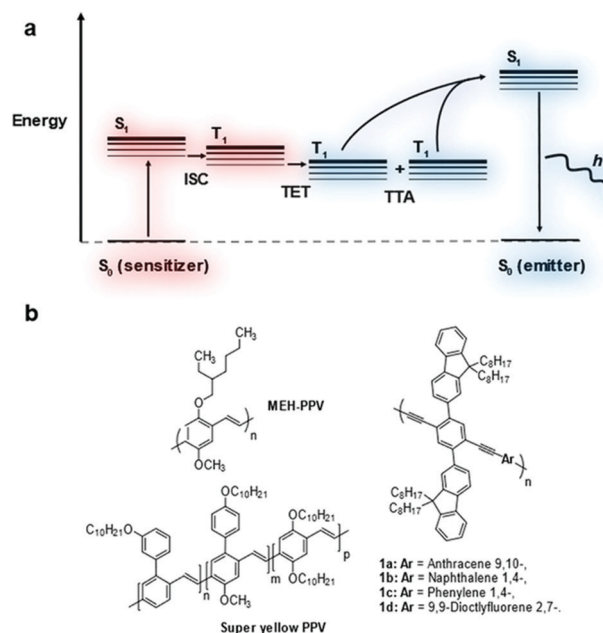


Fig. 1 Jablonski diagram depicting the process involved for TTA-UC (a). Structures of poly(phenylene–vinylene), MEH-PPV and super yellow, and copolymers based on poly(phenylene–ethynylene) investigated as emitters for TTA-UC (b).

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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.¹⁷ The TTA-UC efficiency is measured by the upconversion quantum yield (Φ_{UC}), which is a product of all the quantum yields for photochemical processes involved, given by the equation:

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

where Φ_{ISC} is the intersystem crossing quantum yield, Φ_{TET} is the triplet energy transfer quantum yield, Φ_{TTA} is the TTA quantum yield, and Φ_{PL} is the photoluminescent quantum yield.¹⁶ Φ_{TTA} can be further separated into the contact triplet pair formation efficiency and the factor f ,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.^{18–20}

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

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

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

Herein, the Φ_{UC} of solutions containing commercially available poly(phenylene–vinylene)s, MEH-PPV and super yellow, were measured using an absolute quantum yield method with *meso*-tetraphenyl-tetrabenzoporphine palladium complex (PdTPBP) 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 range in chloroform solution and were optimized for maximum TTA-UC emission.

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.²³ 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

Table 1 Properties of PPE copolymers **1a–d**

	M_w (g mol ⁻¹)	\bar{D}	DP ^a	Abs λ_{max} (nm)	PL λ_{max} (nm)	Φ_{PL} ^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

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

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 stacked packing, 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*-aryldibromide 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⁻¹ (Table 1, see ESI[†] Fig. S7 for GPC traces). 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*-aryldiiodides were used in place of the *para*-aryldibromides **5**. When using Pd(dppf)Cl₂ 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.^{24–26} Higher molecular weights in homopolymers could be obtained by alkyne metathesis,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.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 \sim 320 nm which can be attributed to the fluorene sidechains.²⁸ Copolymer **1a** also showed vibronic features in its absorption and PL spectra reminiscent of the anthracene building block. The Φ_{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 Φ_{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 Φ_{PL} values



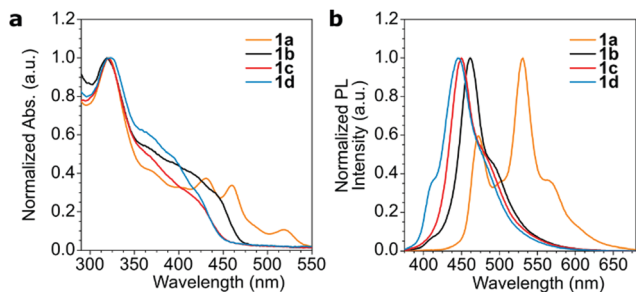


Fig. 2 Normalized UV-Vis absorption (a) and photoluminescence (b) spectra of copolymers **1a–d** in chloroform solution. Excitation wavelength: 350 nm.

typically being in excess of 50%, with many of those containing simple alkyl side chains displaying solution Φ_{PL} close to 100%.^{23,29}

Next, the TTA-UC performance of the polymers were tested with PdTPTBP as the triplet sensitizer. The polymers (0.25 mg mL⁻¹) and the PdTPTBP (7.5 μM) were well-dissolved in chloroform as it was apparent from the absorption spectrum of the samples (Fig. S9, ESI[†]). A red-to-green upconversion was observed with the anthracene-based PPE **1a** with 632 nm excitation (Fig. 3). The upconversion emission intensity was optimized and found to occur using a polymer concentration of 0.25 mg mL⁻¹ with a 7.5 μM 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 band pass filter used on the upconverted emission measurement (Fig. S15, ESI[†]).

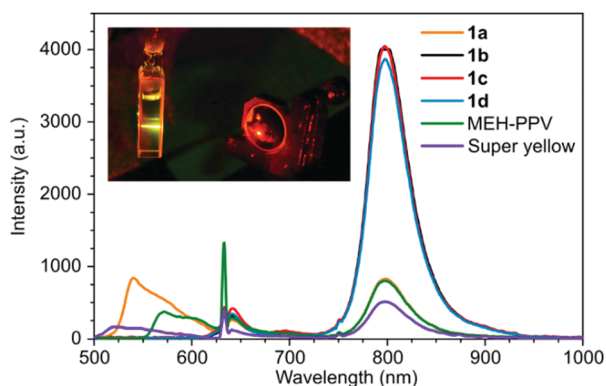


Fig. 3 Emission spectrum of samples containing copolymers **1a–d** (0.25 mg mL⁻¹), MEH-PPV (0.5 mg mL⁻¹), super yellow PPV (0.5 mg mL⁻¹) with PdTPTBP (7.5 μM) as the sensitizer in chloroform solution under 632 nm excitation. Phosphorescence of PdTPTBP was observed at 800 nm and the upconverted emission was observed at 500–600 nm. The insert is a photo of a cuvette containing copolymer **1a** and PdTPTBP showing yellow TTA-UC emission.

These copolymers were then compared to commercially available PPV emitters – MEH-PPV and super yellow – whose Φ_{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 μM . Despite the higher Φ_{PL} of super yellow at 69% compared to 27% for MEH-PPV, its Φ_{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 Φ_{UC} values were measured as a function of the excitation intensity for **1a** and MEH-PPV. A maximum Φ_{UC} value of 0.18% was reached at 8910 mW cm⁻² (Fig. 4). The Φ_{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 Φ_{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 Φ_{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 Φ_{PL} . For **1a** and phenylene-based **1c**,

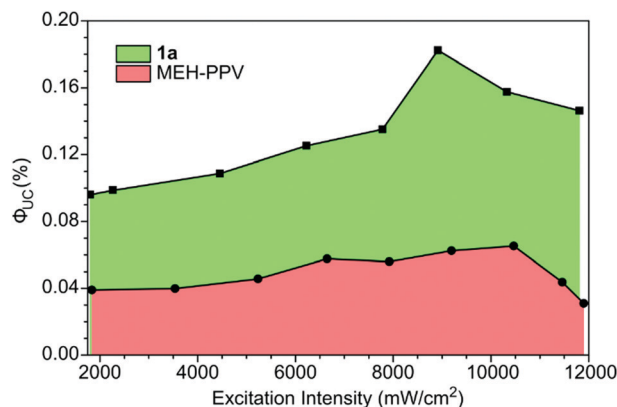


Fig. 4 Dependence of upconversion quantum yield on excitation intensity for PPE **1a** (0.25 mg mL⁻¹), MEH-PPV (0.5 mg mL⁻¹) with PdTPTBP (7.5 μM) as the sensitizer in chloroform solution under 632 nm excitation.



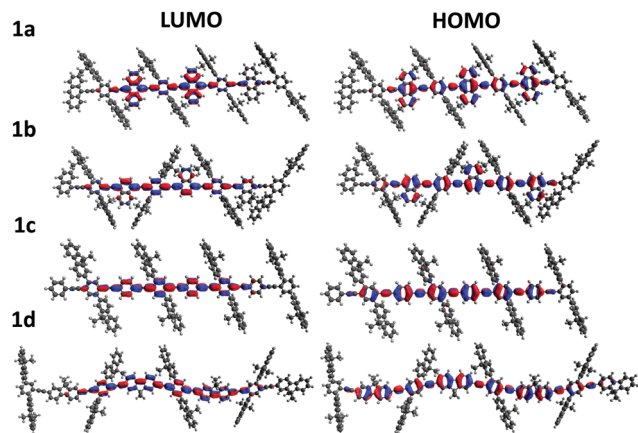


Fig. 5 DFT calculations of model oligomers of **1a–d** displaying the electron probability distributions for the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) for various aryl comonomer units.

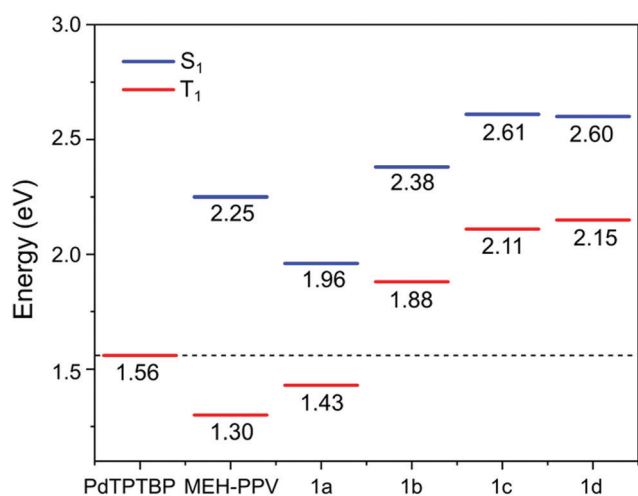


Fig. 6 Energy diagram depicting the calculated singlet and triplet excited state energies obtained by DFT of the model oligomers of **1a–d** compared to the triplet excited state energy of PdTPTBP. The values for MEH-PPV are taken from ref. 34.

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 (S₁) and triplet (T₁) 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 T₁ of 1.51, 2.40 and 2.25 eV were found for the anthracene, phenylene and dioctylfluorene-based polymers respectively.³³ The T₁ values of **1a** and MEH-PPV, at 1.43 eV and 1.30 eV³⁴ respectively, were

lower than T₁ 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 Φ_{UC} measurements after their Φ_{UC} values were determined by absolute quantum yield method. The anthracene-based polymer **1a** outperformed both references achieving maximum Φ_{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

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) <i>meso</i> -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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