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ARTICLE TYPE

Triplet-Triplet Annihilation Upconversion from Rationally Designed Polymeric Emitters with Tunable Inter-Chromophore Distances

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We report an investigation of triplet-triplet annihilation upconversion (TTA-UC) based on polymeric emitters with tunable inter-chromophore distances. Poly[(9-anthrylmethyl methacrylate)-*co*-(methyl methacrylate)] (Poly(AnMMA-*co*-MMA)) with different percentages of AnMMA were synthesized using reversible addition-fragmentation chain transfer (RAFT) polymerization, and used as emitters in association with platinum octaethylporphyrin as sensitizer to form TTA-UC systems. It is observed that TTA-UC intensity first increases with increasing AnMMA percentage in the polymers then decreases, and ultimately disappears, upon further increasing the AnMMA percentage. The results shed light on the key factors affecting TTA-UC in polymers, and have implication to the design of polymer-based TTA-UC systems.

The potential benefits for societal adoption of solar energy are high in comparison to the adverse effects of climate change from using fossil fuels. However, the Shockley-Queisser limit sets a solar power conversion efficiency limit on all single bandgap photovoltaic devices, such as silicon and dye-sensitized solar cells.^[1,2] Triplet-triplet annihilation upconversion (TTA-UC), which can convert the sub-bandgap photons to above-bandgap photons, has been proposed as a way to increase the solar cell efficiency. TTA-UC can be achieved with low power-density (<100 mW/cm²), and non-coherent light as the excitation sources.^[3] Enhancement of solar fuel production of ~130% using a TTA-UC system has been reported in a recent study.^[4]

The TTA-UC process is a sequence of events: a sensitizer becomes excited and reaches a triplet state via intersystem crossing (ISC); triplet-triplet energy transfer (TTET) between sensitizer and emitter; triplet-triplet annihilation (TTA) between two emitters leading to a singlet excited state of one of them; and the final upconverted emission from the singlet excited acceptor (Figure S6 in the Supporting Information).^[5-7] The TTET and TTA steps in the sequence require collisions between two triplets. Thus mobility of the species in the medium is critically important for both the occurrence and efficiency of TTA-UC.

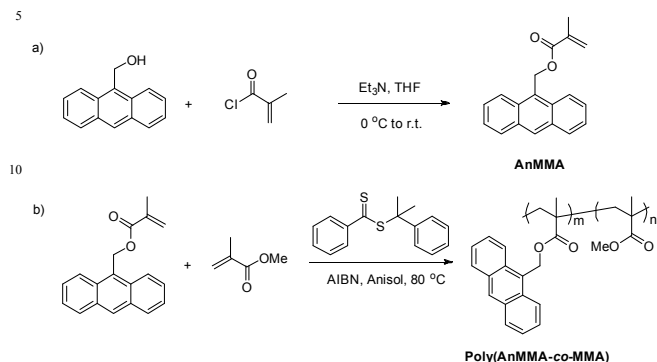
Most studies on TTA-UC are carried out with sensitizers and emitters in solution. Studies on TTA-UC in polymers have also been reported in recent years, with varying degrees of success.^[8-13] The most common strategy is to blend the sensitizer and emitter into a polymer matrix, which merely serves as a

mechanical support for TTA-UC.^[13-15] In addition to the limited mobility of chromophores (sensitizers and/or emitters) in polymers, the bottleneck of this strategy is the solubility and aggregation of chromophores in the polymer. These initial studies led to the proposition that the chromophores be covalently attached to the polymer backbones, which could potentially increase the amount of loaded chromophores in the polymer while avoiding the aggregation or phase separation problem and leading to efficient TTA-UC.^[16] For instance, ruthenium bipyridine and 9,10-diphenylanthracene as polymer core and pendant 'arms', respectively, have been synthesized through reversible addition-fragmentation chain transfer (RAFT) polymerization method, producing both 2-arm and 6-arm polymers containing both sensitizer and emitters in the same polymer. It was observed experimentally that the 2-arm polymer displayed more efficient TTA-UC than the 6-arm counterpart.^[17,18] Still, more experimental results are desired to better understand the key factors involved in TTA-UC in polymers.

Herein, we report an investigation of TTA-UC systems based on polymeric emitters, which possess individual emitters covalently attached to a polymer backbone. Specifically, we used the monomer, 9-anthrylmethyl methacrylate (AnMMA), as individual emitters in copolymers of poly[(9-anthrylmethyl methacrylate)-*co*-(methyl methacrylate)] (Poly(AnMMA-*co*-MMA)), while platinum (II) octaethylporphyrin (PtOEP) as the sensitizer. Our results demonstrate that interactions between chromophores on the same polymer chain play an important role in affecting the overall TTA-UC intensity of these systems.

A series of Poly(AnMMA-*co*-MMA)s with different AnMMA to MMA ratios were synthesized through RAFT polymerization. The monomer, AnMMA, was synthesized by reacting 9-anthracenemethanol with methacryloyl chloride, as shown in Scheme 1a. AnMMA was polymerized with methyl methacrylate (MMA) in a statistical copolymerization with azobisisobutyronitrile (AIBN) as initiator and cumyl dithiobenzoate (CDB) as RAFT chain transfer agent (CTA), shown in Scheme 1b. The use of a copolymer as the polymeric emitter allows us to adjust the distance between the individual AnMMA emitters. MMA is chosen as the co-monomer because it can generate a tertiary carbon propagating radical, matching the reactivity of the AnMMA propagating radical. By varying the molar ratio of AnMMA/MMA in the monomer feed, a series of copolymers were synthesized (Table S1 in the Supporting

Information). Hereafter, we denote the molar ratio of the two monomers, AnMMA/MMA, as AnMMA ratio. Detailed information of synthesis and characterizations are included in the Supporting Information.



Scheme 1. a) Synthesis of AnMMA; and b) synthesis of Poly(AnMMA-co-MMA).

The normalized absorption and fluorescence spectra of Poly(AnMMA-co-MMA) and PtOEP are shown in Figure 1. Note that PtOEP absorbs strongly at 380 nm (Soret band) and 536 nm (Q-band) while emits predominantly at 645 nm (phosphorescence, quantum yield ~0.4).^[19] Poly(AnMMA-co-MMA) does not absorb in the region where PtOEP emits, while emitting at 420 nm, shorter than the Q-band wavelength of PtOEP.

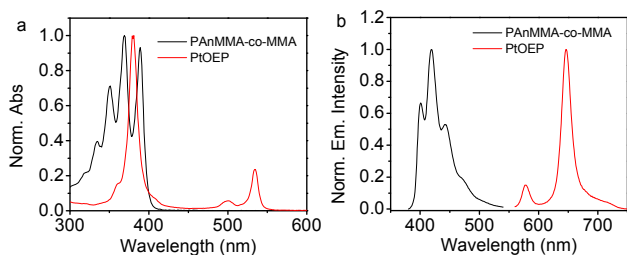


Figure 1. Normalized absorption (a) and emission (b) spectra of Poly(AnMMA-co-MMA) and PtOEP in deoxygenated DMF, respectively, at room temperature.

Poly(AnMMA-co-MMA) and PtOEP were dissolved separately in *N,N*-dimethylformamide (DMF) before being mixed together. The final concentrations of PtOEP and Poly(AnMMA-co-MMA) were as noted later for each mixture. All mixtures were thoroughly deoxygenated by the freeze-pump-thaw method before spectroscopic measurements, which were excited by a 532 nm laser. The double logarithmic plot of the UC intensity measured as a function of the incident laser power (Figure S3) illustrates the transition in the slope from ~2 at lower incident power to ~1 at higher power, similar to what has been reported in the literature.^[20]

Two series of upconversion measurements were carried out. In the first series, the mixtures contained the same concentrations of PtOEP and Poly(AnMMA-co-MMA) with different AnMMA ratios. Results are shown in Figures 2 and S2. With the increase of the AnMMA ratio in the Poly(AnMMA-co-MMA) polymers,

more emitting chromophores (AnMMA) are present in the mixture, and the average distance between the chromophores in the same polymer chain decreases. The probability of collision between chromophore triplets increases, which would be favorable to higher TTA-UC intensity. However, the TTA-UC intensity in this series of mixtures does not increase monotonically with the increase of the AnMMA ratio. It first increases when the AnMMA ratio increases up to ~8.8%, then decreases when the AnMMA ratio increases further, down to almost zero at the AnMMA ratio of 40%. Note that it is unlikely that the chromophores (AnMMA) in these polymers aggregate or have phase separation when the AnMMA ratio increases, as they are covalently attached to the polymer chains and all Poly(AnMMA-co-MMA) polymers disperse well in the solvent. This is supported by the fact that fluorescence spectra of AnMMA in Poly(AnMMA-co-MMA) of different AnMMA ratios (Figure 5) do not show much red-shift when the AnMMA ratio is high. Therefore, simply increasing the number of chromophores in the polymer chain does not always improve the TTA-UC efficiency.

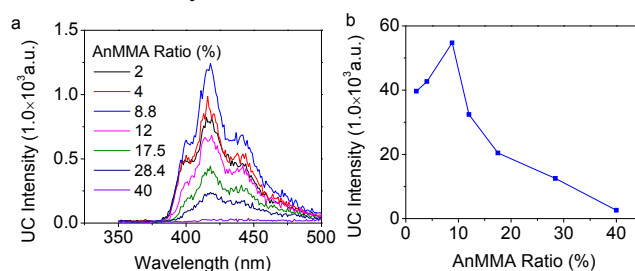


Figure 2. (a) TTA-UC spectra of mixtures containing Poly(AnMMA-co-MMA) (0.25 mM polymer) with different AnMMA ratios and PtOEP (10 μM) in deoxygenated DMF solutions under 532 nm excitation (32 mW/cm²). (b) Relationship of integrated TTA-UC intensity of the mixtures vs. AnMMA ratio.

In the second series, the mixtures contained the same concentrations of PtOEP, while the concentrations of poly(AnMMA-co-MMA) with different AnMMA ratios were adjusted so that all mixtures had the same concentration of the AnMMA unit. Results are shown in Figure 3. Again, the TTA-UC intensity in this series of mixtures first increases when the AnMMA ratio increases up to 4%, then decreases when the AnMMA ratio increases further.

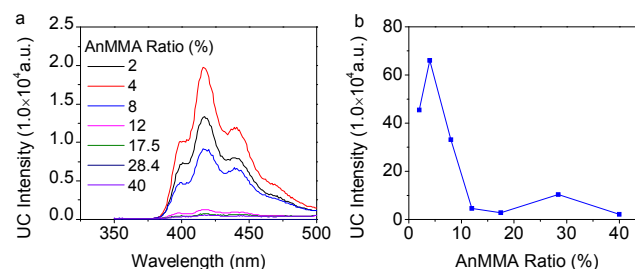


Figure 3. (a) TTA-UC spectra of mixtures containing Poly(AnMMA-co-MMA) (1.5 mM AnMMA unit) with different AnMMA ratios and PtOEP (10 μM) in deoxygenated DMF solutions under 532 nm excitation (32 mW/cm²). (b) Relationship of integrated TTA-UC intensity of the mixtures vs. AnMMA ratio.

Both results indicate that there appears to be an optimal range of the AnMMA ratio in Poly(AnMMA-co-MMA), where the TTA-UC is most efficient. Considering all triplet chromophores (AnMMA) in the mixtures, there are three types of possible collisions among them that could lead to annihilation, as illustrated in the diagram shown in Figure 4: (1) two chromophores attached to two different polymer chains, noted as TTA I, (2) two adjacent chromophores attached to the same polymer chain, noted as TTA II, and (3) two non-adjacent chromophores attached to the same polymer chain, noted as TTA III. TTA I is of inter-chain type, while TTA II and TTA III are of intra-chain type. Under the conditions (excitation power and concentrations of PtOEP and polymer) used in these experiments, it is unlikely that a second triplet sensitization process takes place within the lifetime (Figure S4 in the Supporting information) of the triplet state of AnMMA in the same polymer chain, and the inter-chain TTA can be the only significant UC process occurring (Supporting Information). Yet simply increasing the number of the polymer chains in the mixture does not always increase the observed TTA-UC intensity, as shown in Figure 3. This prompts us to look into the possible self-quenching of the excited singlet of the chromophores.

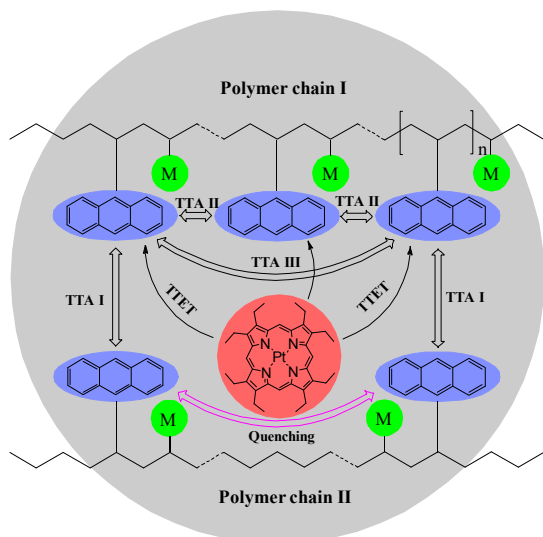


Figure 4. Schematic illustration of collisions among sensitizer and emitters leading to TTA-UC in Poly(AnMMA-co-MMA)/PtOEP mixtures. "M" represents methyl methacrylate.

Fluorescence spectra of the Poly(AnMMA-co-MMA) with different AnMMA ratios directly excited at 360 nm, at either fixed polymer concentration or fixed chromophore concentration, were taken, with results shown in Figure 5. The fluorescence intensity of the polymers of AnMMA ratio >4% decreases as the AnMMA ratio increases, suggesting that self-quenching of excited singlet become significant when the AnMMA ratio is above 4%.

Based on the relationship of the UC intensity vs. AnMMA ratio under the fixed polymer concentration conditions (Figure 2), we attribute the quenching to be mainly due to intra-chain chromophores, and not inter-chain chromophores. This is further supported by results of TTA-UC measurements on PtOEP mixed

with various concentrations of Poly(AnMMA-co-MMA) of 66% AnMMA ratio (Figure S5 in the Supporting Information). Little TTA-UC is observed despite the significant increase in the polymer concentration in the mixture, indicating the dominance of quenching over TTA-UC.

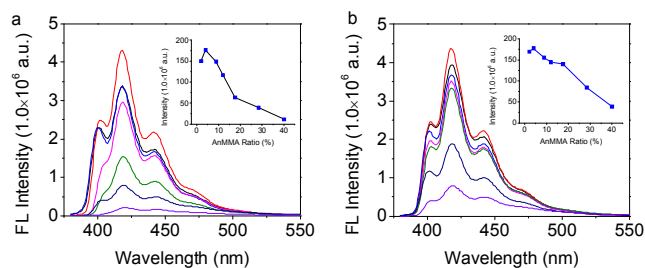


Figure 5. Fluorescence spectra of Poly(AnMMA-co-MMA) with different AnMMA ratios in deoxygenated DMF solutions under 360 nm excitation. (a) Polymer concentrations set at 0.25 mM. (b) AnMMA concentrations set at 1.5 mM. Inserts illustrate the relationship between the integrated intensity and the AnMMA ratio.

These results combine to suggest that the observed UC intensity is directly related to the net abundance of the excited singlet of the chromophores. The generation of the excited singlet of the chromophores is ascribed to the inter-chain TTA, while its quenching is due to the intra-chain interaction. In other words, TTA I processes promote UC while interaction among excited singlets in the same polymer suppress UC, and the amount of AnMMA in the polymer (and hence overall in the mixture) controls the observed UC intensity. At low AnMMA ratios, the intra-chain quenching is negligible, and increasing AnMMA ratio is conducive to increasing the observed UC intensity. At high AnMMA ratios, the intra-chain quenching of the excited singlet of the chromophores becomes predominant, resulting in very low UC intensity regardless of the total polymer concentration. Therefore, a window exists of optimal AnMMA ratios where TTA-UC is maximal. Such ratio varies slightly in the two series of experiments shown here, which can be understood as follows. At fixed polymer concentration, generation of the excited singlets of the chromophores increases with increasing AnMMA ratio. The decrease in UC intensity after AnMMA ratio of 8.8% reflects the predominance of intra-chain quenching of the excited singlets. In contrast, when the concentration of the AnMMA unit in the polymers is fixed, the polymer concentration decreases, leading to the reduced generation of the excited singlets, as the AnMMA ratio increases. The effect on both generation and quenching of the excited singlets results in a smaller optimal AnMMA ratio of ~4%.

We therefore suggest that, when designing and synthesizing polymeric emitters to be used in the TTA-UC systems to achieve high UC efficiency, it is important to consider the distance between the adjacent chromophores to avoid self-quenching of the excited singlet of the emitter, more so than simply increasing the number of emitting chromophores per polymer chain. One simple way to test whether self-quenching occurs is to measure the prompt fluorescence of the polymers.

In summary, we report the design and synthesis of a series of

Poly[(9-anthrylmethyl methacrylate)-*co*-(methyl methacrylate)] through RAFT with different AnMMA ratios, resulting in tunable inter-chromophore distances. These polymers can serve as emitters, with PtOEP as sensitizer, in TTA-UC systems. TTA-UC intensity of the Poly(AnMMA-*co*-MMA)/PtOEP mixtures displays interesting dependence on the AnMMA ratio in the polymer. It increases initially with increasing AnMMA ratio, and decreases after the AnMMA ratio is above an optimal value, ultimately disappearing when AnMMA ratio reaches 40%. Interactions between chromophores on the same polymer chain play the key role in affecting the TTA-UC intensity in these systems. It is critical to minimize intra-chain chromophore quenching in order to achieve high UC intensity.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details. See DOI: 10.1039/b000000x/

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