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

Xinjun Yu, Xian Cao, Xiaoping Chen, Neil Ayres and Peng Zhang

Materials

All chemicals were purchased from Sigma-Aldrich at the highest available purity and used as received unless otherwise stated. ¹H and ¹³C NMR measurements were performed in CDCl₃, with Si(CH₃)₄ standard, using a 400 MHz Bruker Ultrashield (100 MHz for ¹³C). ¹H NMR and ¹³C NMR spectra were analyzed with MestReNova software. Fourier transform infrared (FTIR) spectra were collected on a Nicolet 6700 spectrometer and analyzed with OMIC 32 software. Mass spectrometry was performed using a Micromass Q-TOF-2TM spectrometer.

Synthesis of 9-anthrylmethyl methacrylate (AnMMA)

9-Anthracenemethanol (4.00 g, 19.2 mmol), triethylamine (5.80 g, 57.4 mmol) were added to 100 mL THF in a round-bottom flask equipped with septum and stir bar. The mixture was cooled in ice bath for 30 min. Methacryloyl chloride (6.00 g, 57.4 mmol) was added to the flask through a syringe dropwise at 0 °C. The reaction was allowed to proceed under room temperature overnight. THF was removed by vacuum distillation, and the residue dissolved in CH₂Cl₂ and washed with 1 M HCl solution, NaHCO₃ solution and brine. The solution was dried over Na₂SO₄ and then concentrated to afford the crude product which was purified using column chromatograph on silica gel (silica gel 60 Å, 70–230 mesh) with DCM:Hexane (3:1 v/v) as the

mobile phase. The solvent was removed and the product dried in vacuum to yield 4.0 g of yellow powder. Yield: 70%. ¹H NMR (CDCl₃): δ (ppm) 1.92 (s, 3 H, OCH₃), 5.51(s, 1 H, C=CH₂), 6.05(s, 1 H, C=CH₂), 6.22 (s, 2 H, CH₂O),7.48–7.51 (t, 2 H, *J* = 8.0 Hz, aromatic H), 7.56–7.59 (t, 2 H, *J* = 8.0 Hz, aromatic H), 8.03–8.05 (t, 2 H, *J* = 8.0 Hz, aromatic H), 8.37–8.39 (t, 2 H, *J* = 8.0 Hz, aromatic H), 8.52 (s, 1 H, aromatic H). ¹³C NMR (CDCl₃): δ (ppm) 167.64 (*C*=O), 136.25, 131.51, 131.23, 129.26, 126.72, 126.52, 126.17, 125.22, 124.17 (sp²–C), 59.28 (CH₂O), 18.50 (C=CH₂CH₃). FT-IR (cm⁻¹): v_(NH) = 3325, v_(CH) = 2930. MS (TOF MS ES+): 299.1057 M+Na⁺ (Calculated: 299.1048).

Synthesis of poly[(9-anthrylmethyl methacrylate)-*co*-(methyl methacrylate)] (Poly(AnMMA-*co*-MMA))

General procedure for polymerization:

For the polymerization of Poly(AnMMA-*co*-MMA) with a 15/85 mol ratio of AnMMA and MMA in the feed, the procedure is as follows: 9-anthrylmethyl methacrylate (1.0 g, 3.6 mmol), methyl methacrylate (2.20 mL, 20.5 mmol), cumyl dithiobenzoate (65.6 mg, 0.240 mmol), azobisisobutyronitrile (AIBN, 13 mg, 0.08 mmol) and 8 mL anhydrous THF were added to a round bottom flask. The reaction flask was sealed with a rubber septum and purged with N_2 for 30 min. The reaction was allowed to proceed at 80 °C for 21 h and stopped by exposure the reaction to air. The residue was then precipitated in cold methanol twice to afford pink solids. AIBN was used to remove thiocarbonylthio groups from the prepared polymers. Equal mass AIBN and polymer were dissolved in anisole and purged with N_2 for 30 min. The reaction was allowed to proceed at 80 °C for 20 min. The reaction was allowed to proceed at 80 °C for 30 min. The reaction was used to remove thiocarbonylthio groups from the prepared polymers. Equal mass AIBN and polymer were dissolved in anisole and purged with N_2 for 30 min. The reaction was allowed to proceed at 80 °C for 20 min. The reaction was allowed to proceed at 80 °C for 20 min. The reaction was allowed to proceed at 80 °C for 20 min. The reaction was allowed to proceed at 80 °C for 20 min. The reaction was allowed to proceed at 80 °C for 20 min.

afford the final polymer as white power. The polymerization of the other copolymers was performed under identical conditions with the appropriate amounts of AnMMA and MMA.

Mole feed ratio	3/97	4/96	6/94	10/90	10/90	20/80	25/75	60/40
M _n (x10 ⁴)	1.53	1.46	1.59	1.43	1.82	1.86	1.85	1.98
PDI	1.02	1.10	1.03	1.07	1.03	1.06	1.10	1.05
Actual ratio	2/98	4/96	8.8/91.2	12/88	17.5/82.5	28.4/71.6	40/60	66/34

Table S1. Characteristics of Poly(AnMMA-co-MMA) copolymers.

Spectroscopic measurements

Absorption spectra were collected with a Cary 50 Bio UV-Vis spectrophotometer.

Photoluminescence (PL) spectra were collected on a home-built setup as shown in Figure S1. The system consists of a 532-nm DPSS laser (85-GCB-020, Melles Griot) and some optical elements (shutter, attenuator, microscopic objective and optical fibers), a monochromator (Acton Research) and a photon counting PMT (Hamamatsu R928P), data acquisition electronics & software (NCL and SpectraSense, Acton Research), and a PC. Laser stray-light was reduced by using a 532 nm notch filter placed in front of the entrance to the monochromator.

The laser beam was focused onto the polished end of a 400- μ m silica step-index optical fiber (NA = 0.22, RoMack, Inc.) with a microscope objective (10×, NA = 0.25, Newport). The shutter and the variable neutral density filter (Newport) were used to adjust the laser intensity at the samples. Laser power was attenuated to 1.0 mW (or as noted in the figures) at the sample position, focused onto a spot of 2 mm in diameter. Samples were contained in a quartz vial placed in front of the fiber. All experiments were carried out at room temperature.



Figure S1. Schematic of instrumental setup.

Time-decay PL measurements were carried on a setup, which includes a 532-nm laser powered by a function generator (Atten 20B) and modulated by a rectangular waveform of 40 Hz from the same function generator, a photomultiplier tube (Hamamatsu R928P) placed at the exit port of the monochromator (Acton Research, SpectroPro 500i), and a digital oscilloscope. The down slope of the modulation was used to trigger the oscilloscope, which monitored the output from the photomultiplier. Laser stray-light was reduced by using a 532 nm notch filter placed in front of the entrance to the monochromator. All of the measurements were performed at room temperature.

Sample preparation for spectroscopic measurements

All samples were prepared in the following manner. 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.

<u>Estimation of concentration of triplet chromophores in the PtOEP/Poly(AnMMA-co-MMA)</u> mixture

Under steady state conditions the concentration of triplets can be estimated, assuming that the concentration of triplet species is much lower than ground state species and that triplet species decay mainly through first-order processes. Take [PtOEP] = 10 μ M, [AnMMA chromophore] = 1.5 mM, excitation power density = 32 mW/cm², and the first-order rate constant ~10⁴ s. Molar extinction coefficient of PtOEP is taken as 10⁵ M⁻¹cm⁻¹. ^[S5] The excitation rate of PtOEP is thus calculated to be ~ 40 s⁻¹, and concentration of the triplet chromophores in the mixture, [AnMMA chromophore*], to be ~40 nM. Compare this value to the concentration of polymer in the mixture, 0.25 mM, and one concludes that the possibility of having more than one triplet chromophore in a single polymer chain is extremely low. Therefore, upconversion in the mixture is ascribed to the inter-chain TTA of chromophores.

Determination of TTA-UC quantum yield of PtOEP/ Poly(AnMMA-co-MMA) mixtures

TTA-UC quantum yield of the PtOEP/Poly(AnMMA-*co*-MMA) mixtures was determined by using Eq. S1 below, following procedures described previously.^[S1]

$$\phi_{unk} = 2\phi_{std} \left(\frac{A_{std}}{A_{unk}}\right) \left(\frac{I_{unk}}{I_{std}}\right) \left(\frac{\eta_{unk}}{\eta_{std}}\right)^2$$
(S1)

where Φ , A, I and η represent the upconversion quantum yield, absorbance, integrated photoluminescence intensity from the spectra and refractive index, respectively. Subscript std denotes a reference fluorophore of known quantum yield and subscript unk the sample to be determined. Rose Bengal (RB) is used as the reference fluorophore in this study (Φ std = 0.11 for RB in ethanol at room temperature under 532 nm excitation).^[S2] The refractive indices of DMF and ethanol at 532 nm are η (DMF) = 1.428 and η (EtOH) = 1.361.^[S3,S4] The integrated intensity of the upconversion was measured in the region of 350-500 nm while that of rhodamine B was measured in the region of 550-700 nm. All measurements were carried out under the same experimental settings. Results are shown in Figures S2.



Figure S2. Emission spectra (a) and quantum yield (b) of mixtures containing Poly(AnMMA-*co*-MMA) (1.5 mM AnMMA unit) with different AnMMA ratios and PtOEP (10 μ M) in deoxygenated DMF solutions under 532 nm excitation (32 mW/cm²). Emission spectra (c) and quantum yield (d) of mixtures containing Poly(AnMMA-*co*-MMA) (0.25 mM polymer) with different AnMMA ratios and PtOEP (10 μ M) in deoxygenated DMF solutions under 532 nm excitation (32 mW/cm²).



Figure S3. Excitation power dependence of upconversion (left) and PtOEP phosphorescence (right) of Poly(AnMMA-*co*-MMA) with 12% AnMMA (0.25 mM)/PtOEP (10 μ M) in deoxygenated DMF, respectively, at room temperature.



Figure S4. Decay times of upconversion emission (420 nm) and PtOEP phosphorescence emission (645 nm) of Poly(AnMMA-*co*-MMA) with different AnMMA ratios (0.25 mM)/PtOEP (10 μ M) in deoxygenated DMF, respectively, at room temperature, excited at 532 nm (32 mW/cm²).



Figure S5. TTA-UC spectra of PtOEP (25 μ M) mixed with different concentrations of Poly(AnMMA-*co*-MMA) (AnMMA ratio = 66%) in deoxygenated DMF at room temperature, excited at 532 nm (32 mW/cm²).



Figure S6. Schematic of TTA-UC of PtOEP/Poly(AnMMA-co-MMA) mixture.





Figure S9. Mass spectrum of 9-anthrylmethyl methacrylate.

REFERENCES

- [S1] Cao, X.; Hu, B.; Zhang, P. J. Phys. Chem. Lett. 2013, 4, 2334-2338.
- [S2] Seybold, P.G.; Gouterman, M.; and Callis, J. Photochem. Photobiol. 1969, 9, 229-242.
- [S3] Aminabhavi, T. M.; Gopalakrishna, B. J. Chem. Eng. Data. 1995, 40, 856-861.

[S4] Washburn, E. W.; West, C. J.; Dorsey, N. E.; Ring, M. D. International Critical Tables of Numerical Data. Physics, Chemistry, and Technology, 1st ed. **1930**, Vol. 7.

[S5] Bansal, A.K.; Holzer, W.; Penzkofer, A.; Taiju, T. Chemical Physics. 2006, 330, 118-129.