Electronic Supplementary Material (ESI) for Materials Advances.

The performance of conjugated polymers as emitters for triplet-triplet annihilation upconversion

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General experimental

Commercial reagents were purchased from Univar, Sigma-Aldrich, AK Scientific, Matrix Scientific, Ajax Finechem, and Labchem, and were used as received. Anhydrous toluene, diethyl ether, dichloromethane, and tetrahydrofuran were obtained from alumina drying columns. For reactions carried out under inert conditions, standard Schlenk techniques were used. Solvents were sparged with nitrogen gas for several hours prior to use, and the reaction vessels were sealed with a rubber septum under a nitrogen atmosphere. Thin layer chromatography (TLC) was done using Merck-Millipore Silica gel glass plates (60G F_{254}), with a 254 nm and 365 nm light mercury lamp used for identifying spots.

^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were obtained in $CDCl_3$, on a 400 MHz Varian spectrometer. NMR peaks were referenced to the $CHCl_3$ solvent peak.

X-ray diffraction intensity data were collected with a Rigaku Synergy Diffractometer using either Cu-Ka radiation with the temperature during data collection maintained at 100 K using an Oxford Cryosystems cooling device. The structures were solved by direct methods and difference Fourier synthesis. Thermal ellipsoid plots were generated using the program Mercury integrated within the WINGX suite of programs.

DFT calculations performed using Gaussian 16, Revision B.01.

GPC data was obtained on a GPC/SEC from Agilent Technologies, calibrated with narrow polystyrene standards. Run in HPLC grade chloroform at 35 ^{o}C, with a RID and a diode array detector with channels set to 300, 400 and 500 nm.

Synthesis and characterisation

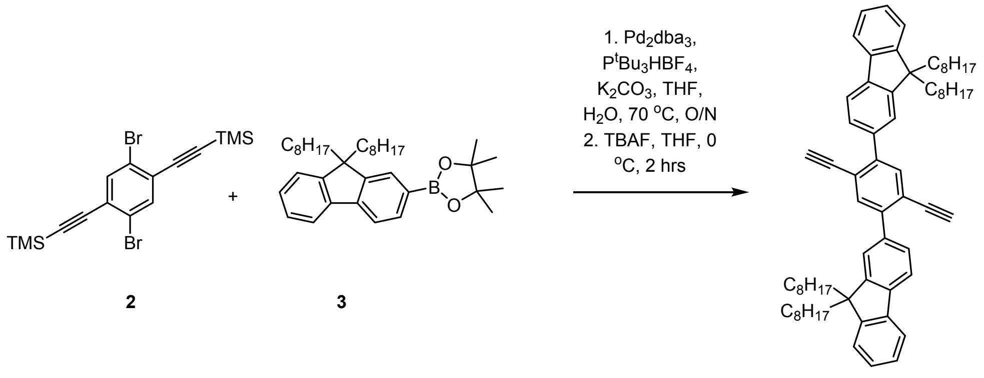


Figure S1 Synthesis of 2,2'-(2,5-diethynyl-1,4-phenylene)bis(9,9-dioctyl-9H-fluorene) **4**.

2-(9,9-dioctyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.52 g, 6.8 mmol), ((2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(trimethylsilane) (0.976 g, 2.28 mmol), potassium carbonate (2.78 g, 20 mmol), Tris(dibenzylideneacetone)dipalladium(0) (0.234 g, 0.255 mmol), and Tri-tert-butylphosphonium tetrafluoroborate (0.215 g, 0.738 mmol) were dissolved in 60 mL of degassed THF and 20 mL of degassed water. The mixture was then stirred at room temperature for 30 mins. Then the mixture was heated to 70 °C overnight. The mixture was then extracted in chloroform and washed with water, the organic layer was then collected and dried over magnesium sulfate and filtered through a thin layer of silica. The solvent was then evaporated, and the crude product was then redissolved in 30 mL of dry THF and cooled to 0 °C. A 1M solution of tetrabutylammonium fluoride (6.75 mL) was then added dropwise and the solution was stirred at 0 °C for 2 hours. The mixture was then diluted with hexanes and filtered through a thin layer of silica. The solvent was the evaporated and the product was loaded onto cellite. The product was then purified by DCVC eluting with 0, 1, 2, 5, 10% DCM in hexanes.

Mass = 1.53g (74%)

^{1}H NMR (400 MHz, $CHCl_3$, δ): 7.76 (m, 6H), 7.68 (s, 2H), 7.54 (d, *J* = 7.3Hz, 2H), 7.34 (m, 6H), 3.09 (s, 2H), 2.00 (m, 8H), 1.12 (m, 46H), 0.82 (t, *J* = 7.1Hz, 13H), 0.70 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.09, 150.39, 143.37, 140.87, 140.71, 137.57, 134.93, 127.66, 127.19, 126.78, 124.04, 122.86, 121.12, 119.83, 119.43, 82.95, 81.47, 55.17, 40.38, 31.77, 30.12, 29.27, 29.26, 23.80, 22.58, 14.05; HRMS (ESI) *m/z*: $[M]^+$ calcd for $C_{68}H_{86}$, 902.6730; found, 902.6730.

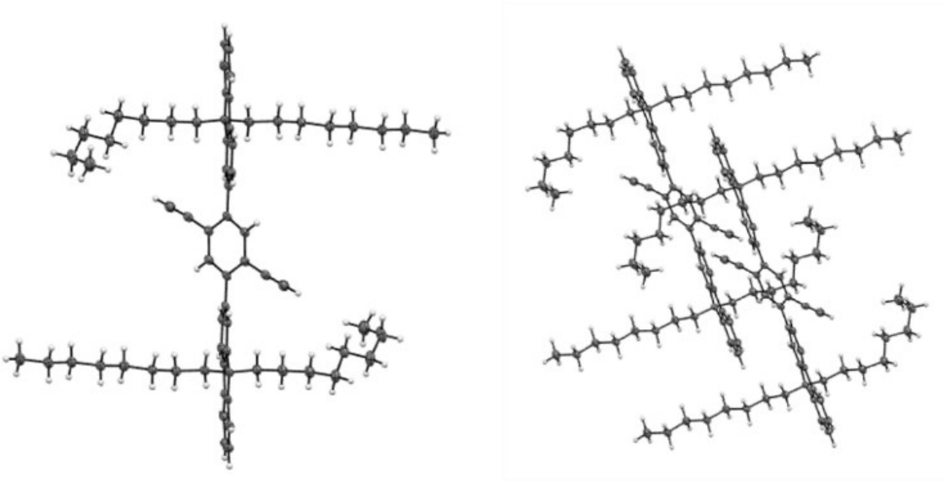


Figure S2 Single crystal structure and packing for 2,2'-(2,5-diethynyl-1,4-phenylene)bis(9,9-dioctyl-9H-fluorene) **4**.

Table S1 Crystal data and structure refinement for 2,2'-(2,5-diethynyl-1,4-phenylene)bis(9,9-dioctyl-9H-fluorene) **4**.

Empirical formula	$C_{68}H_{86}$	
Formula weight	903.36	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.5616(3) Å	a= 101.674(2)°.
	b = 11.0936(3) Å	b= 97.846(2)°.
	c = 15.1256(4) Å	g = 91.063(2)°.
Volume	1392.15(7) Å^3	
Z	1	
Density (calculated)	1.078 Mg/m^3	
Absorption coefficient	0.443 mm^{-1}	
F(000)	494	
Crystal size	0.290 x 0.060 x 0.039 mm^3	
Theta range for data collection	3.014 to 77.171°.	
Index ranges	-9<=h<=10, -13<=k<=14, -19<=l<=18	
Reflections collected	17183	
Independent reflections	5702 [R(int) = 0.0690]	
Completeness to theta = 67.684°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.65435	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5702 / 0 / 309	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0555, wR2 = 0.1412	
R indices (all data)	R1 = 0.0740, wR2 = 0.1534	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.284 and -0.246 e.Å^{-3}	

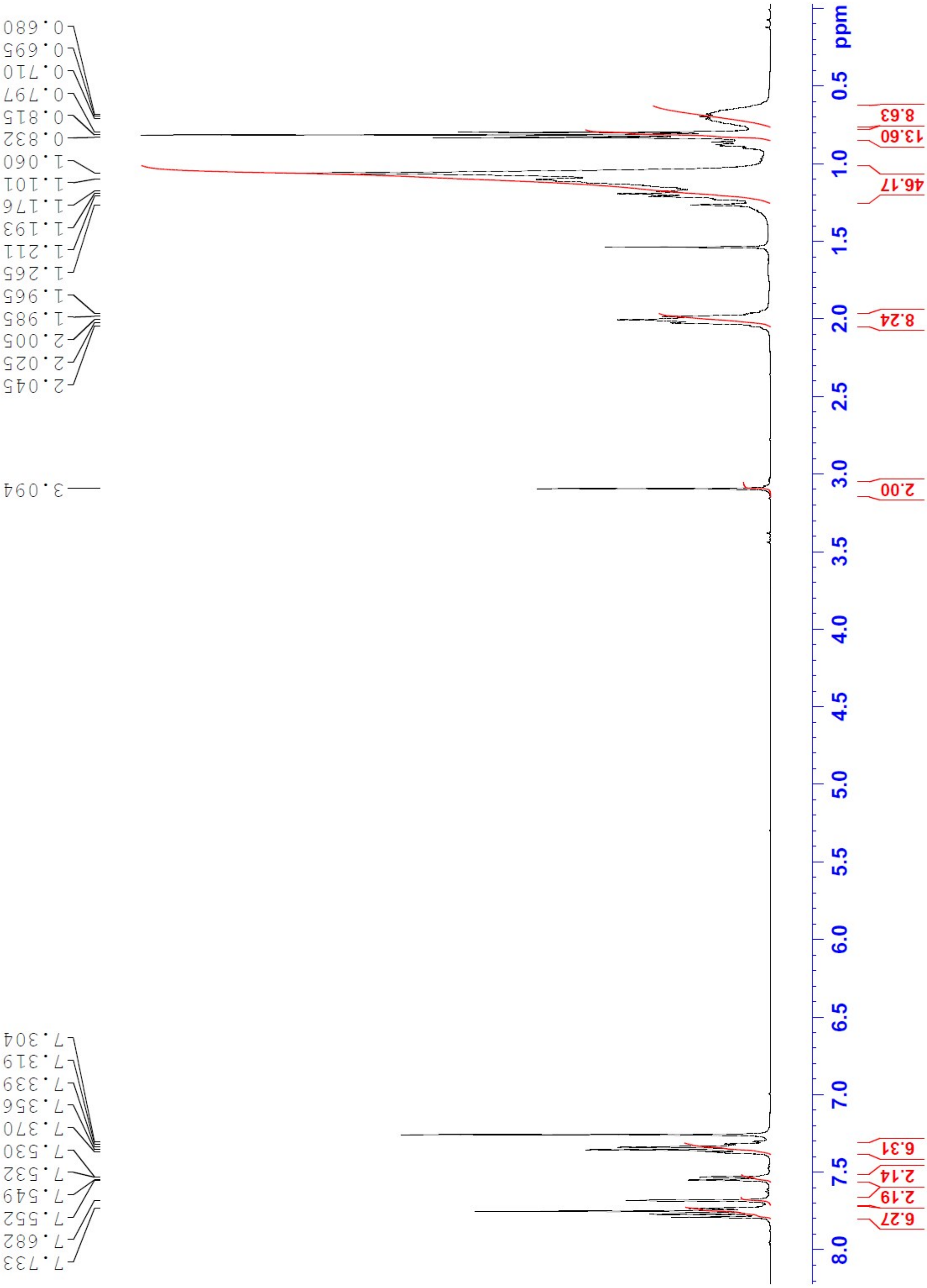


Figure S3 1H NMR spectra of 2,2'-(2,5-diethynyl-1,4-phenylene)bis(9,9-dioctyl-9H-fluorene) **4**.

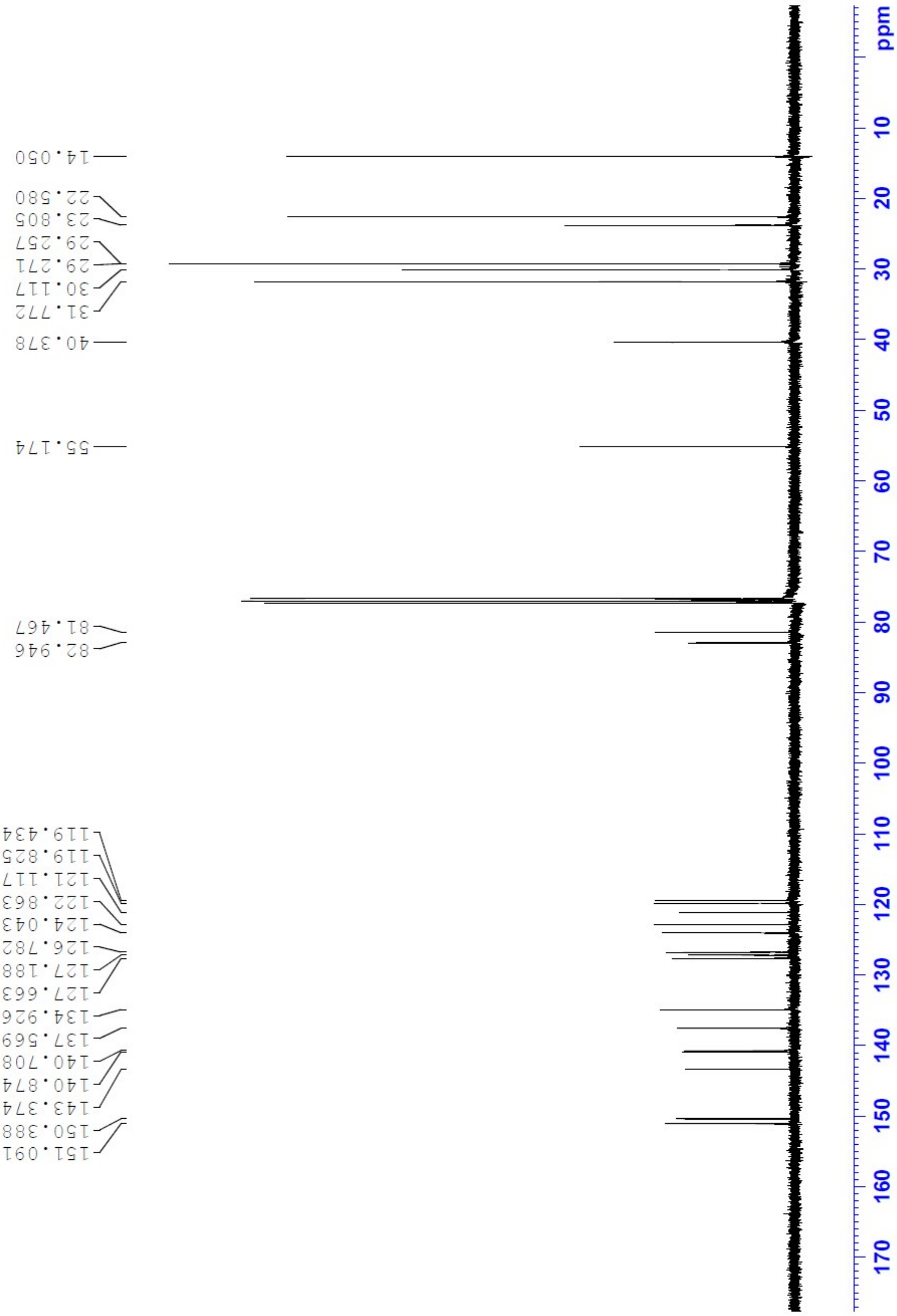


Figure S4 13C NMR spectra of 2,2'-(2,5-diethynyl-1,4-phenylene)bis(9,9-dioctyl-9H-fluorene) **4**.

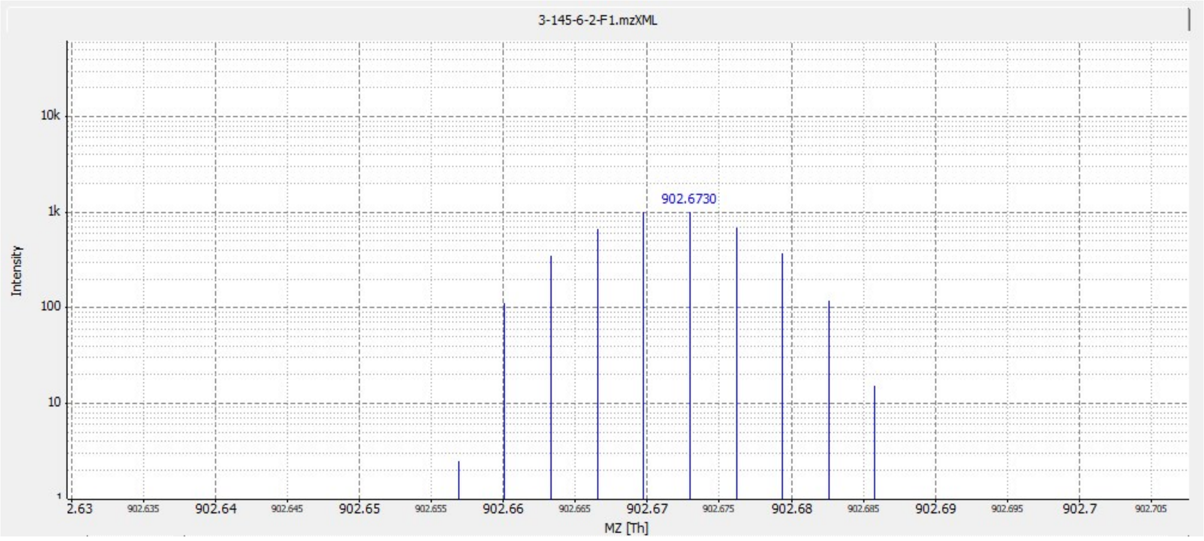
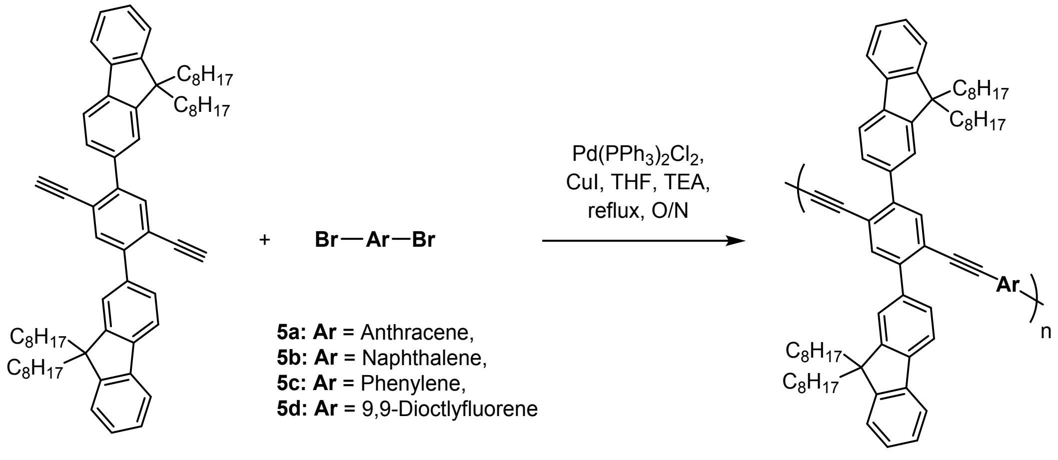


Figure S5 HRMS spectra of 2,2'-(2,5-diethynyl-1,4-phenylene)bis(9,9-dioctyl-9H-fluorene) **4**.



5a: Ar = Anthracene,
5b: Ar = Naphthalene,
5c: Ar = Phenylene,
5d: Ar = 9,9-Dioctlyfluorene

1a: Ar = Anthracene,
1b: Ar = Naphthalene,
1c: Ar = Phenylene,
1d: Ar = 9,9-Dioctlyfluorene

Figure S6 Synthesis of copolymers **1a-d**.

General polymerization method:

2,2'-(2,5-diethynyl-1,4-phenylene)bis(9,9-dioctyl-9H-fluorene) (0.2 g, 0.22 mmol), Dibromoaryl comonomer (0.22 mmol), bis(triphenylphosphine)palladium(II) dichloride (50 mg, 0.07 mmol), and copper(I) iodide (30 mg, 0.15 mmol) were dissolved in 4 mL of degassed THF and 4 mL of degassed triethylamine. The mixture was then heated to reflux overnight. The mixture was then diluted in hexanes and washed with saturated aqueous ammonium chloride. The organic layer was then collected and filtered through silica. The solvent was then evaporated, and the polymer was redissolved in THF and precipitated into methanol with vigorous stirring. The mixture was then centrifuged, and the polymer was washed three times with methanol.

Example procedure:

2,2'-(2,5-diethynyl-1,4-phenylene)bis(9,9-dioctyl-9H-fluorene) (0.2 g, 0.22 mmol), 1,4-dibromobenzene (51.9 mg, 0.22 mmol), bis(triphenylphosphine)palladium(II) dichloride (50 mg, 0.07 mmol), and copper(I) iodide (30 mg, 0.15 mmol) were dissolved in 4 mL of degassed THF and 4 mL of degassed triethylamine. The mixture was then heated to reflux overnight. The mixture was then diluted in hexanes and washed with saturated aqueous ammonium chloride. The organic layer was then collected and filtered through silica. The solvent was then evaporated, and the polymer was redissolved in THF and precipitated into methanol with vigorous stirring. The mixture was then centrifuged, and the polymer was washed three times with methanol.

Mass = 88.2mg (41%)

Table S2 Reaction yields for PPE copolymers **1**.

Aryl spacer	**Polymer yield**
Anthracene **1a**	66%
Naphthalene **1b**	44%
Phenylene **1c**	41%
Dioctylfluorene **1d**	56%

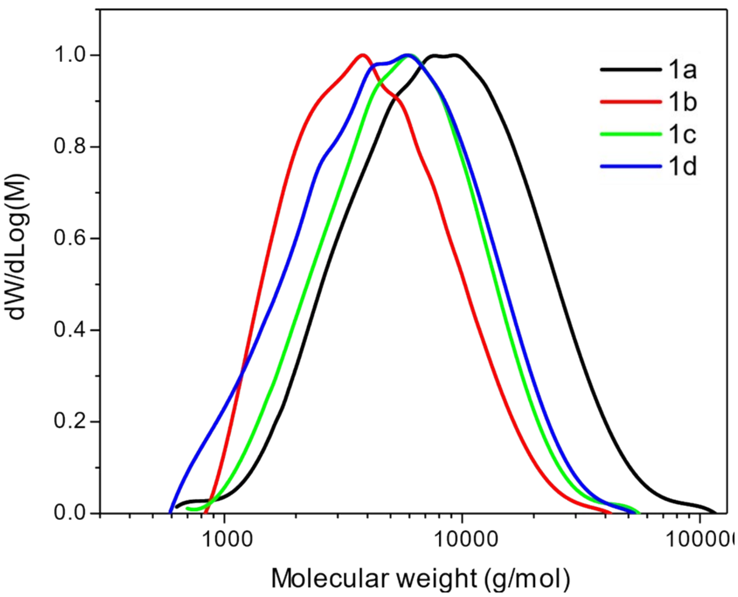


Figure S7 GPC traces for copolymers **1a-d**.

Photophysical measurements and data

UV-Vis Spectroscopy was performed on Agilent Technologies Cary 50 UV-Vis. Photoluminescence spectroscopy was performed on Varian Cary Eclipse fluorimeter. Absolute photoluminescence quantum yield of the samples was determined via an integrating sphere method using an integrating sphere accessory (F3018, Horiba Jobin Yvon) on a Fluorolog-3 fluorimeter. Upconversion samples were degassed three times prior to analysis. Upconversion spectra were taken using an Ocean Optics USB spectrometer with 300 µm fiber optic cable. Absolute upconversion quantum yield measurements were taken via an integrating sphere method with a LABSPHERE (model number: 4P-GPS-053-SL) and detection with a liquid nitrogen cooled CCD camera from Princeton Instruments (series number: SP2500).

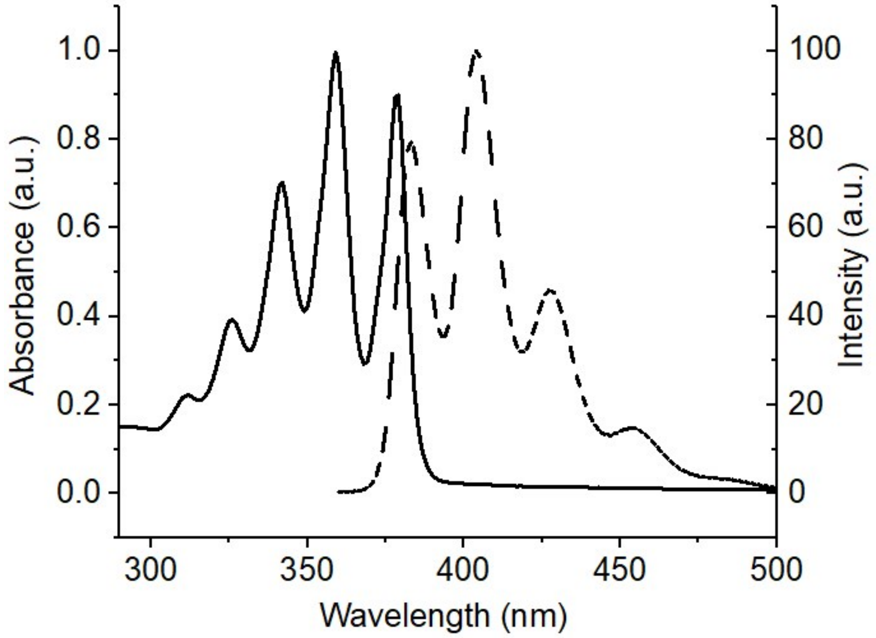


Figure S8 Normalized solution UV-Vis absorbance spectra (solid line) and photoluminescence spectra (dashed line) for Anthracene quantum yield standard.

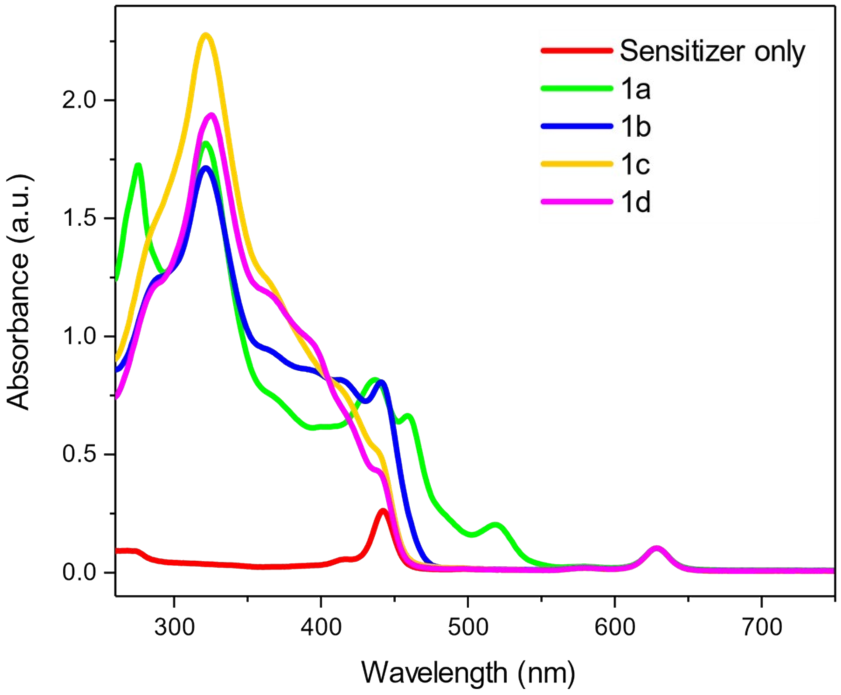


Figure S9 Solution UV-Vis absorbance spectra of polymer upconversion samples, polymer concentration = 0.25 mg/mL, PdTPTBP (sensitizer) concentration = 7.5 μM, path length = 0.1 cm.

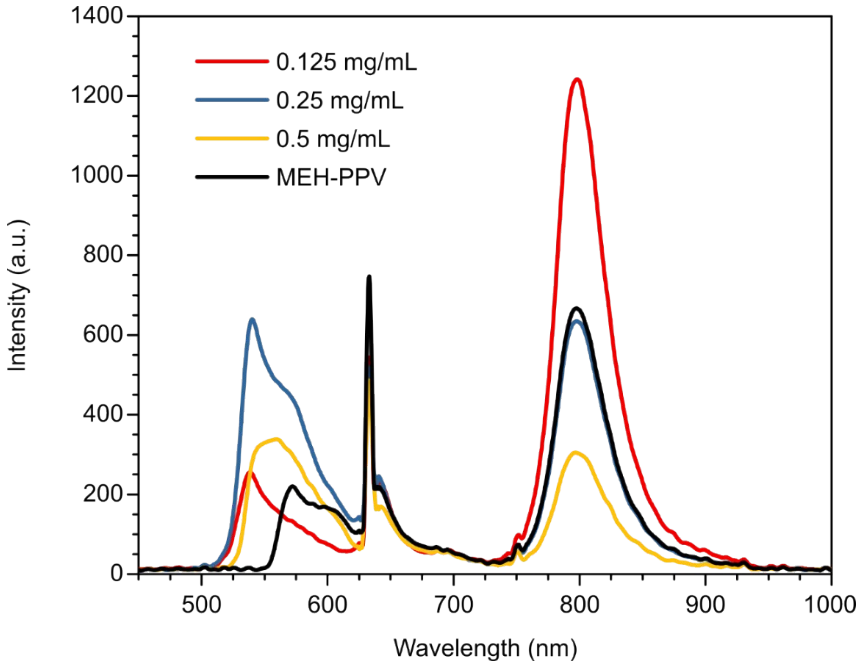


Figure S10 Variation of PPE copolymer **1a** (anthracene) concentration with fixed sensitizer (PdTPTBP) concentration = 7.5 µM, MEH-PPV = 0.5 mg/mL, 800 ms integration time, 632 nm excitation.

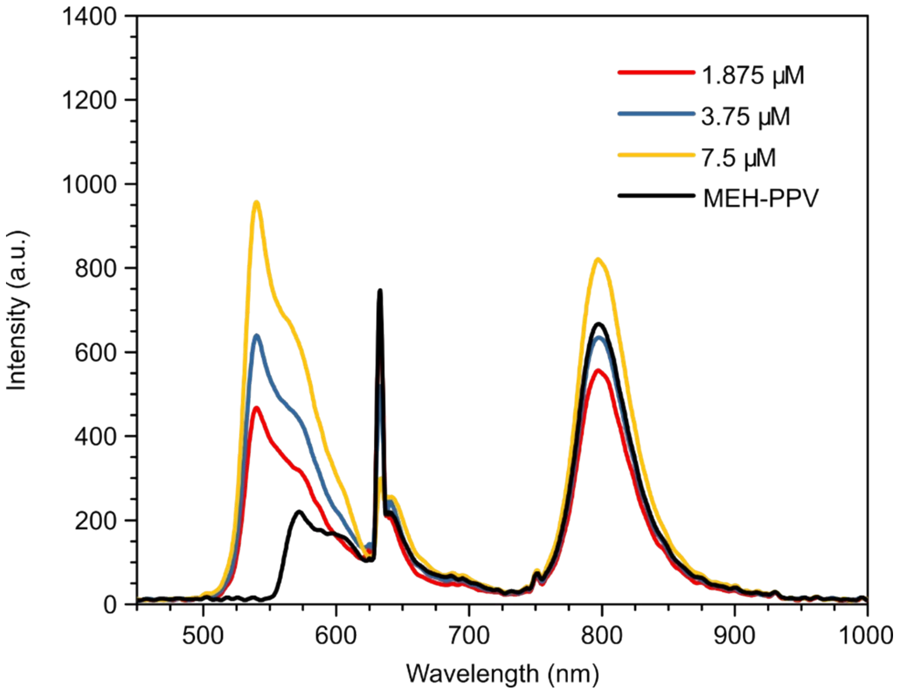


Figure S11 Variation of sensitizer (PdTPTBP) concentration with fixed PPE copolymer **1a** (anthracene) concentration = 0.25 mg/mL, MEH-PPV = 0.5 mg/mL, 800 ms integration time, 632 nm excitation.

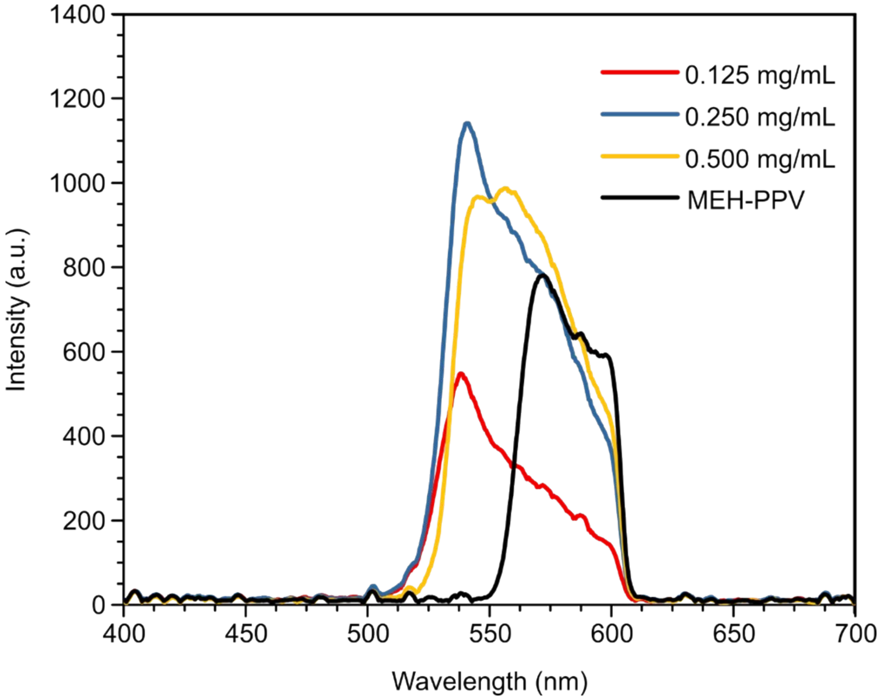


Figure S12 Variation of PPE copolymer **1a** (anthracene) concentration with fixed sensitizer (PdTPTBP) concentration = 7.5 µM, MEH-PPV = 0.5 mg/mL, 2000 ms integration time, 632 nm excitation, with a 600 nm low band pass filter.

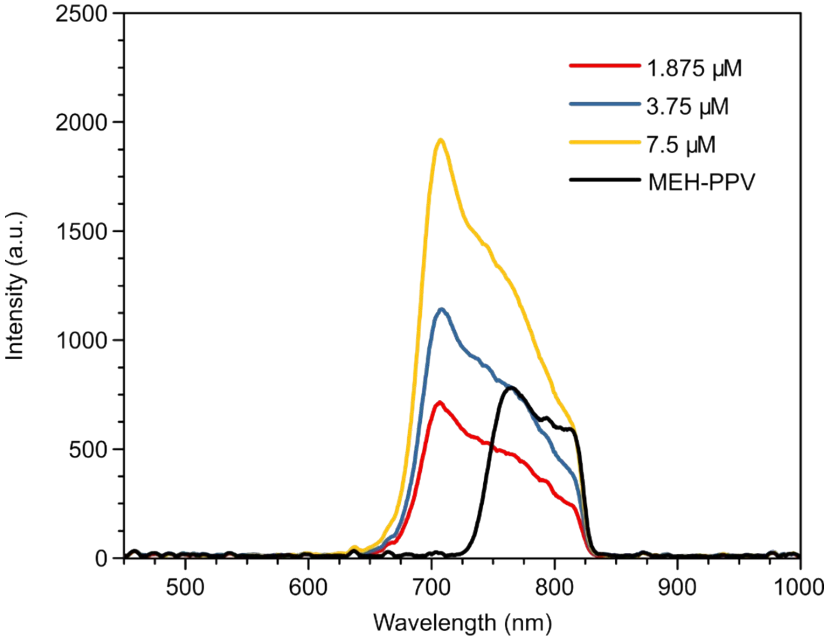


Figure S13 Variation of sensitizer (PdTPTBP) concentration with fixed PPE copolymer **1a** (anthracene) concentration = 0.25 mg/mL, MEH-PPV = 0.5 mg/mL, 2000 ms integration time, 632 nm excitation, with a 600 nm low band pass filter.

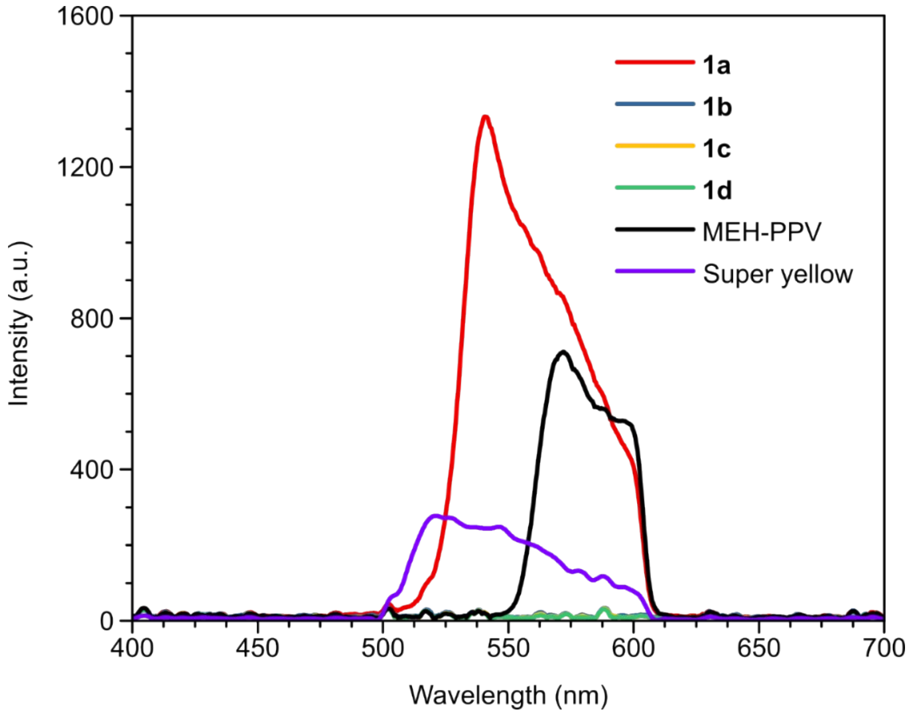


Figure S14 Upconverted emission from PPE copolymers **1,** MEH-PPV = 0.5 mg/mL, Super Yellow PPV = 0.5 mg/mL, PdTPTBP = 7.5 µM, PPE copolymer concentration = 0.25 mg/mL, 2000 ms integration time, 632 nm excitation, with a 600 nm low band pass filter.

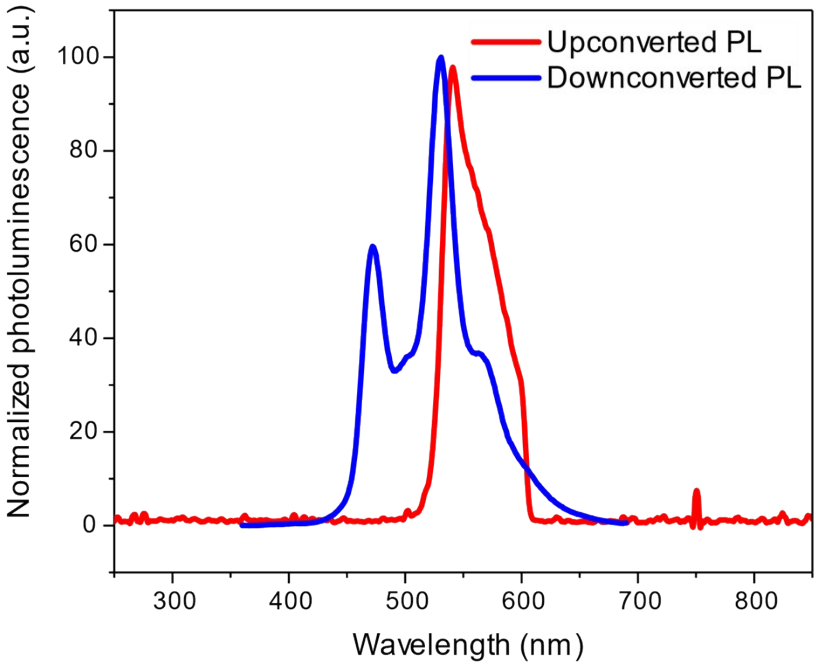


Figure S15 Normalized upconverted emission from PPE copolymer **1a,** copolymer concentration = 0.25 mg/mL, 2000 ms integration time, 632 nm excitation, with a 600 nm low band pass filter, plotted against downconverted photoluminescent emission taken with 350 nm excitation in chloroform solution.

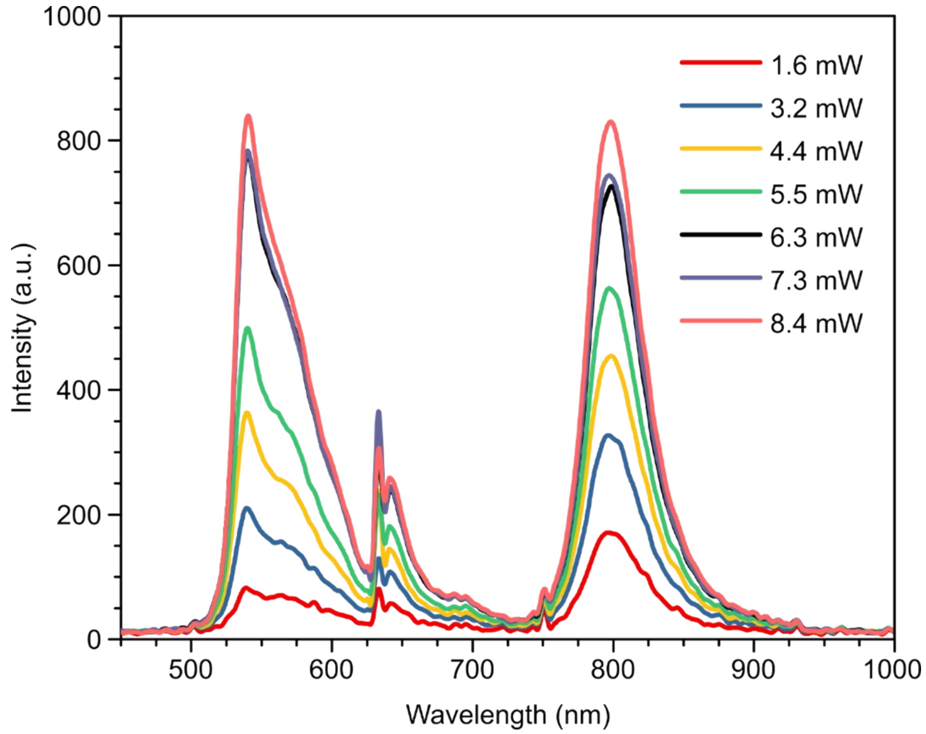


Figure S16 Variation of excitation intensity with PPE copolymer **1a** (anthracene, 0.25 mg/mL) and PdTPTBP (7.5 µM), MEH-PPV = 0.5 mg/mL, 800 ms integration time, 632 nm excitation.

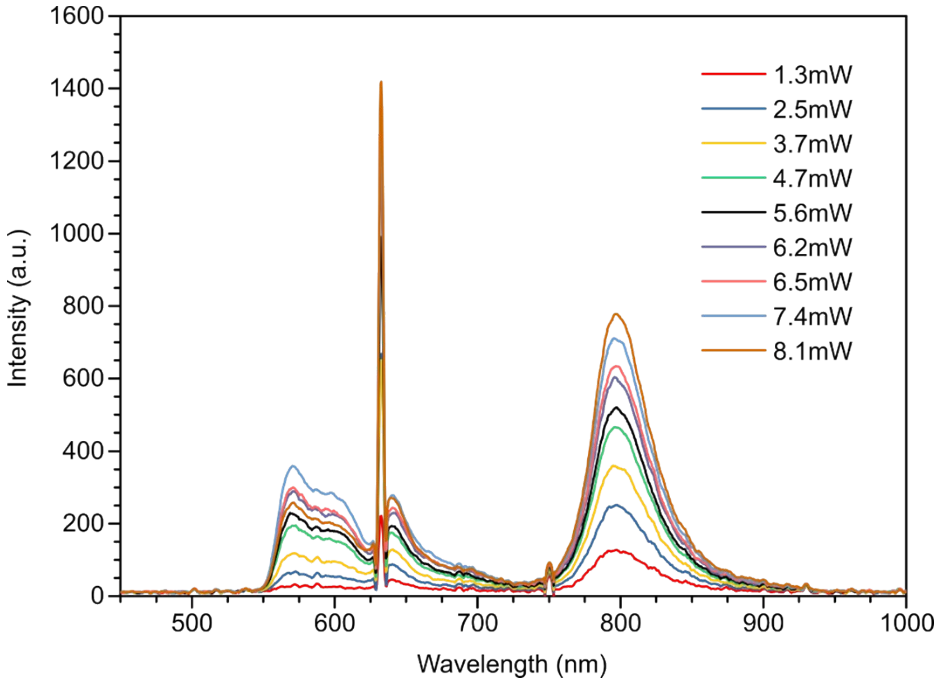


Figure S17 Variation of excitation intensity with MEH-PPV (0.5 mg/mL) and PdTPTBP (7.5 µM), 800 ms integration time, 632 nm excitation.

Table S3 Summary of Φ_{UC} data for Anthracene **1a** and MEH-PPV, measured relative to the values determined via integrating sphere; MEH-PPV = 0.039% and Super yellow = 0.029%.

Polymer	**Excitation (mW/cm²)**	**% Φ_{UC} (relative to MEH-PPV)**	**% Φ_{UC} (relative to SUPER YELLOW)**	**Relative error**
1a	2263	0.098	0.101	0.003
	4456	0.108	0.111	0.003
	6224	0.125	0.128	0.003
	7780	0.135	0.138	0.003
	8912	0.182	0.186	0.004
	10327	0.157	0.161	0.004
	11812	0.146	0.149	0.003
MEH-PPV	1839	0.039	0.039	0.000
	3536	0.039	0.040	0.001
	5234	0.045	0.046	0.001
	6649	0.057	0.059	0.002
	7922	0.055	0.057	0.002
	8771	0.062	0.064	0.002
	9195	0.065	0.063	0.002
	10468	0.043	0.066	0.023
	11459	0.031	0.044	0.013