

SUPPLEMENTARY INFORMATION

Rationally Designed Singlet Sink for Glassy Polymeric Photon
Upconverting Films

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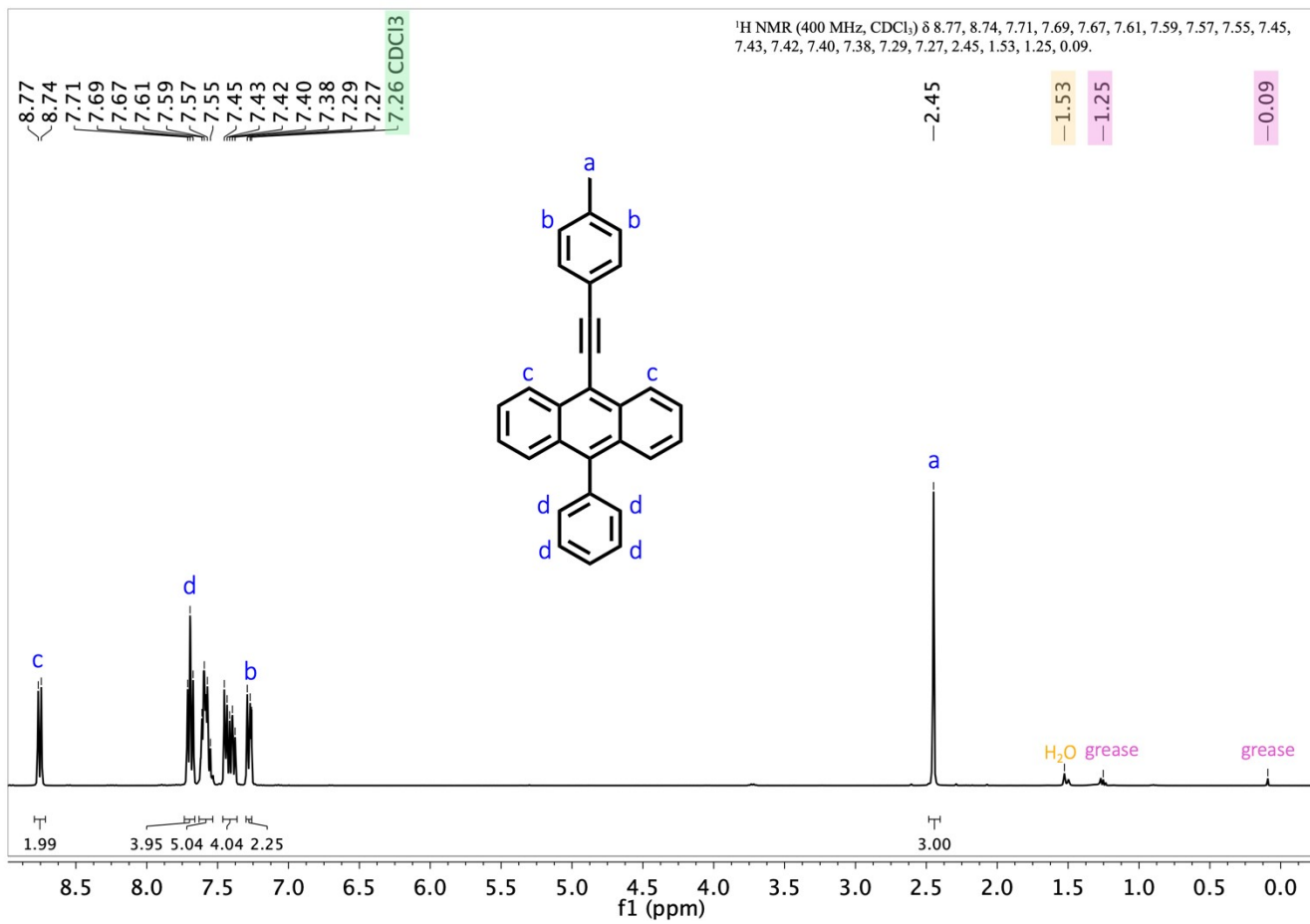


Figure S1. ¹H NMR spectroscopy of PTEA.

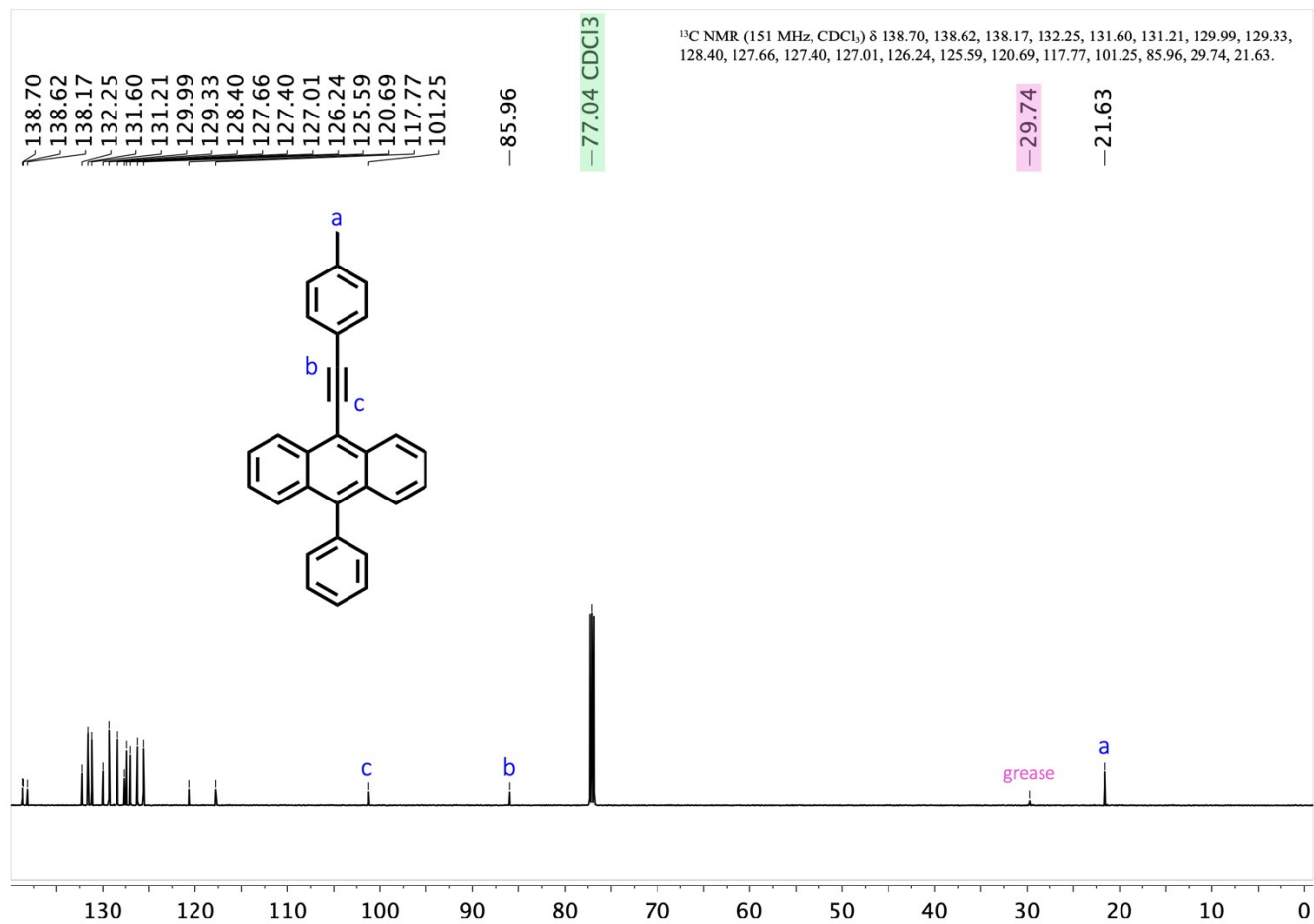


Figure S2. ¹³C NMR spectroscopy of PTEA.



Figure S3. Custom-made mechanical hot-press used for sample preparation in N₂ glovebox. Surface area: 100 x 40 mm. Heating power: 240 W (top and bottom heating elements have capability of being controlled separately). Pressing force: ~100 kg/cm². Heating temperature capability: from room temperature up to 300 °C.

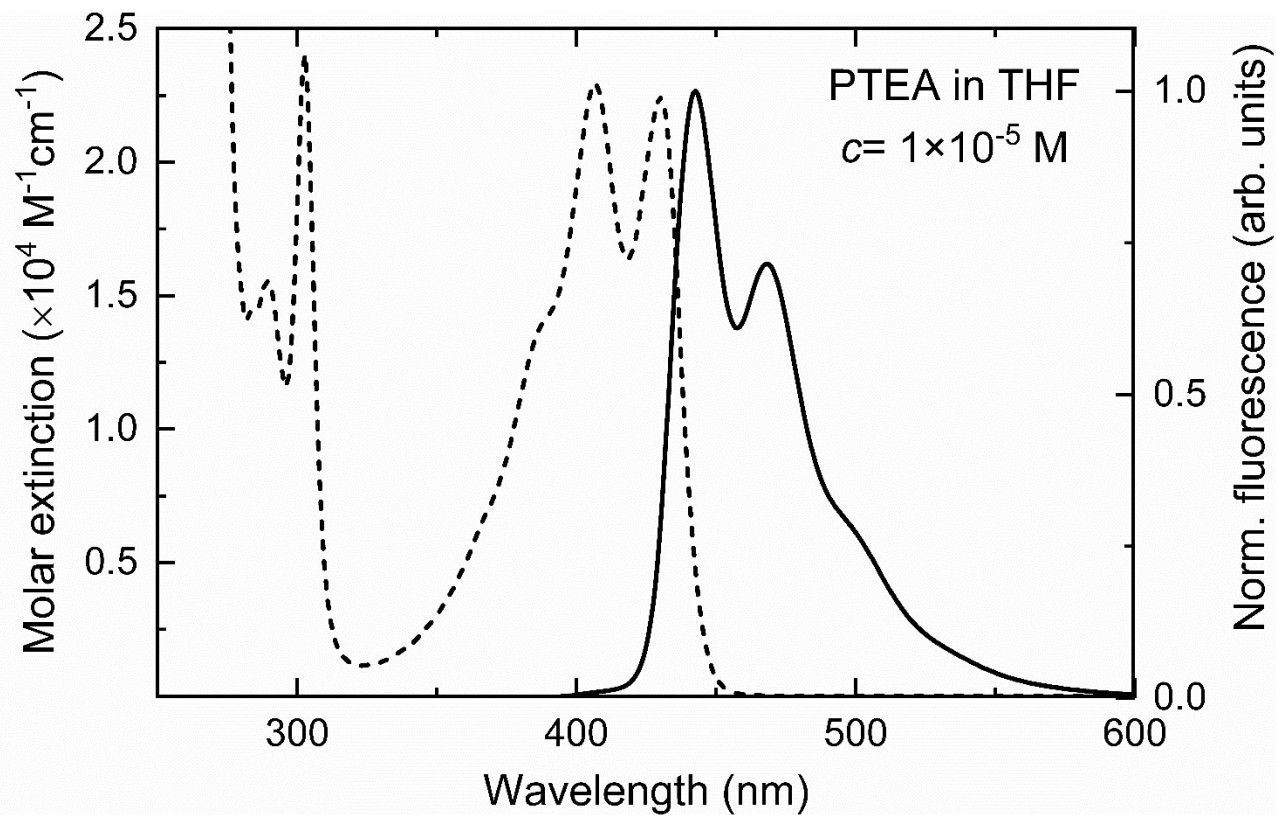


Figure S4. Molar extinction and normalized fluorescence spectra of PTEA ($1 \times 10^{-5} \text{ M}$) in THF. Excitation wavelength for fluorescence: 375 nm. Maximum molar extinction coefficient (MEC) at 407 nm = $2.30 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. MEC at 430 nm = $2.24 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$

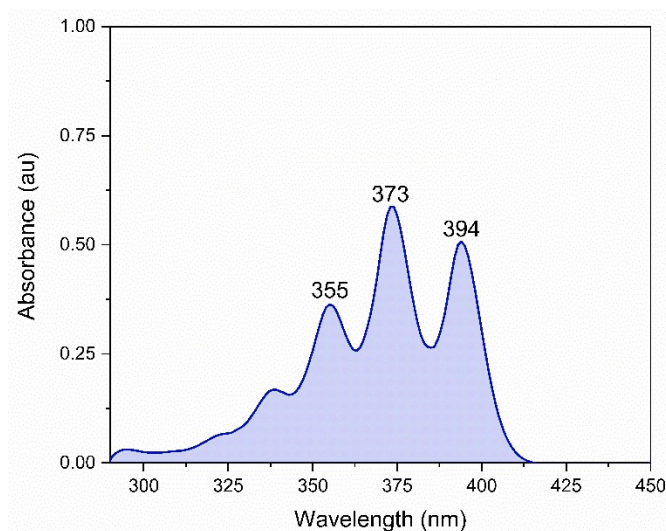


Figure S5. Absorbance profile of DPA in THF ($c = 4 \cdot 10^{-5}$ M) by UV-Vis spectroscopy.

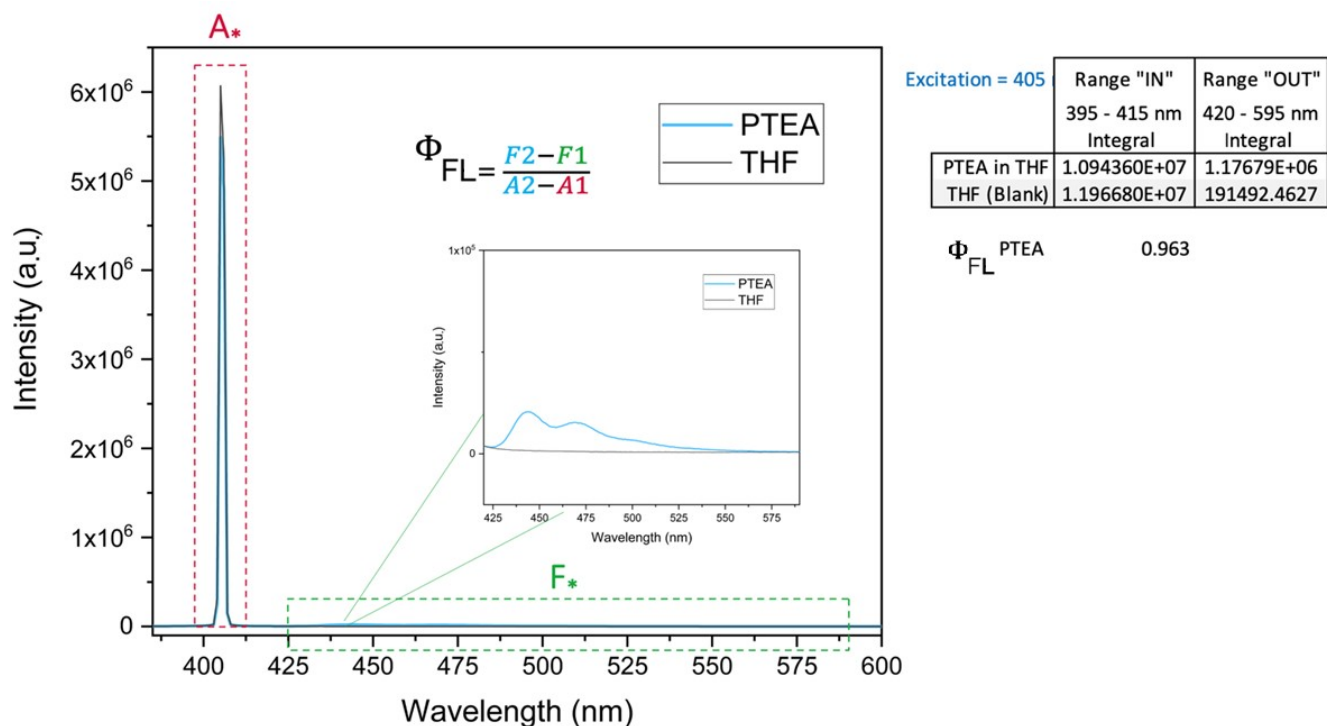


Figure S6. Absolute fluorescence quantum yield (Φ_{FL}) of PTEA in THF. The Φ_{FL} of PTEA was measured at a concentration of 10^{-5} M by integrating sphere technique with a Horiba Scientific K-Sphere by exciting at 405 nm using a 90° angle geometry. F_2 = integral of PTEA photoluminescence from 420 nm – 595 nm. F_1 = integral of THF photoluminescence from 420 nm – 595 nm. A_2 = integral of PTEA excitation from 395 – 415 nm. A_1 = integral of THF excitation from 395 nm – 415 nm.

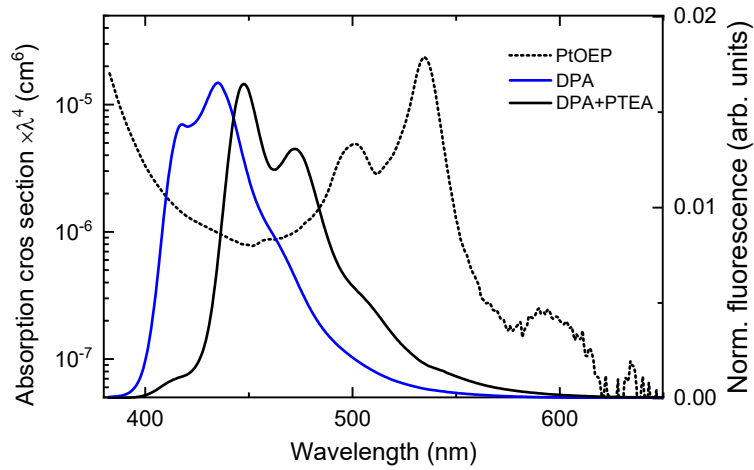


Figure S7. Absorption cross section of PtOEP (multiplied by λ^4) in PMMA at 0.05 wt% and fluorescence spectra of UC films of DPA(40wt%)/PtOEP(0.05wt%)/PMMA and PTEA(0.25wt%)/DPA(40wt%)/PtOEP(0.05wt%)/PMMA. Excitation for fluorescence – 375 nm. Fluorescence spectra are normalized to integrated spectral area.

Our calculations of the overlap integral (J) for PTEA \rightarrow PtOEP and DPA \rightarrow PtOEP in UC films containing 0.05 wt% PtOEP, 40 wt% DPA and varying concentration (0-0.5 wt%) of PTEA confirm that J is larger for PTEA ($J_{\text{PTEA}}=[1.8\text{-}2.1]\times 10^8 \text{ nm}^6$) compared to DPA ($J_{\text{DPA}}=1.5\times 10^8 \text{ nm}^6$). Calculation results are provided in Table R1 below.

Table S1. Förster energy transfer rate calculation of UC films with 40wt% DPA, 0.05 wt% PtOEP and 0-0.5 wt% PTEA.

No.		PTEA conc. wt%	$J^{(1)}$ nm ⁶	$\Phi_{\text{FL}}^{(2)}$ %	$R_0^{(3)}$ nm	$d^{(4)}$ nm	$\tau^{(5)}$ ns	$k_{\text{F}}^{(6)}$ s ⁻¹
1	DPA \rightarrow PtOEP	0	$1.5\cdot 10^8$	18	2.77	1.05	3.8	$8.8\cdot 10^9$
2		0.025	$1.8\cdot 10^8$	27	3.05	11.4	4.6	$8.0\cdot 10^3$
3	PTEA \rightarrow PtOEP	0.05	$1.9\cdot 10^8$	35	3.21	10.1	4.8	$2.1\cdot 10^4$
4		0.1	$2.0\cdot 10^8$	35	3.25	8.84	4.8	$5.1\cdot 10^4$
5		0.25	$2.0\cdot 10^8$	44	3.38	7.46	5.4	$1.6\cdot 10^5$
6		0.5	$2.1\cdot 10^8$	43	3.39	6.13	5.2	$5.4\cdot 10^5$

1) Spectral overlap integral. 2) Fluorescence quantum yield. 3) Förster radius. 4) distance between

emitter/annihilator and PtOEP, $d = \sqrt[3]{\frac{1}{(c_{donor} + c_{acceptor}) \cdot N_A}}$, where $c = \frac{wt \cdot \rho}{M}$ (M – molar mass, ρ – density, $\rho=1.18 \text{ g/cm}^3$ was used in calculations). 5) singlet state lifetime. 6) Förster rate.

Spectral overlap integral $J(\lambda)$ calculated by: $J(\lambda) = \int \lambda^4 F_D(\lambda) \sigma_A(\lambda) d\lambda$,

where λ is the wavelength, F_D is the normalized fluorescence spectrum, and σ_A is absorption cross-section.

Förster radius calculated by:

$$R_0 = \sqrt[6]{\frac{9\Phi_{FL}\kappa^2}{128\pi^5 n^4} J(\lambda)},$$

where Φ_{FL} is the fluorescence quantum yield, κ is dipole orientation factor (κ was assumed to be $0.845\sqrt{2/3}$ for amorphous film with randomly oriented dipoles. [M. Z. Maksimov, I. M. Rozman, Opt. Spectrosc. 1962, 12, 337.]), n is the refraction index.

Förster rate:

$$k_F = \frac{1}{\tau} \left(\frac{R_0}{d} \right)^6.$$

Despite shifting the emission spectrum away from the PtOEP Soret band, introducing PTEA also increases the overlap with its Q band, leading to a slightly larger J .

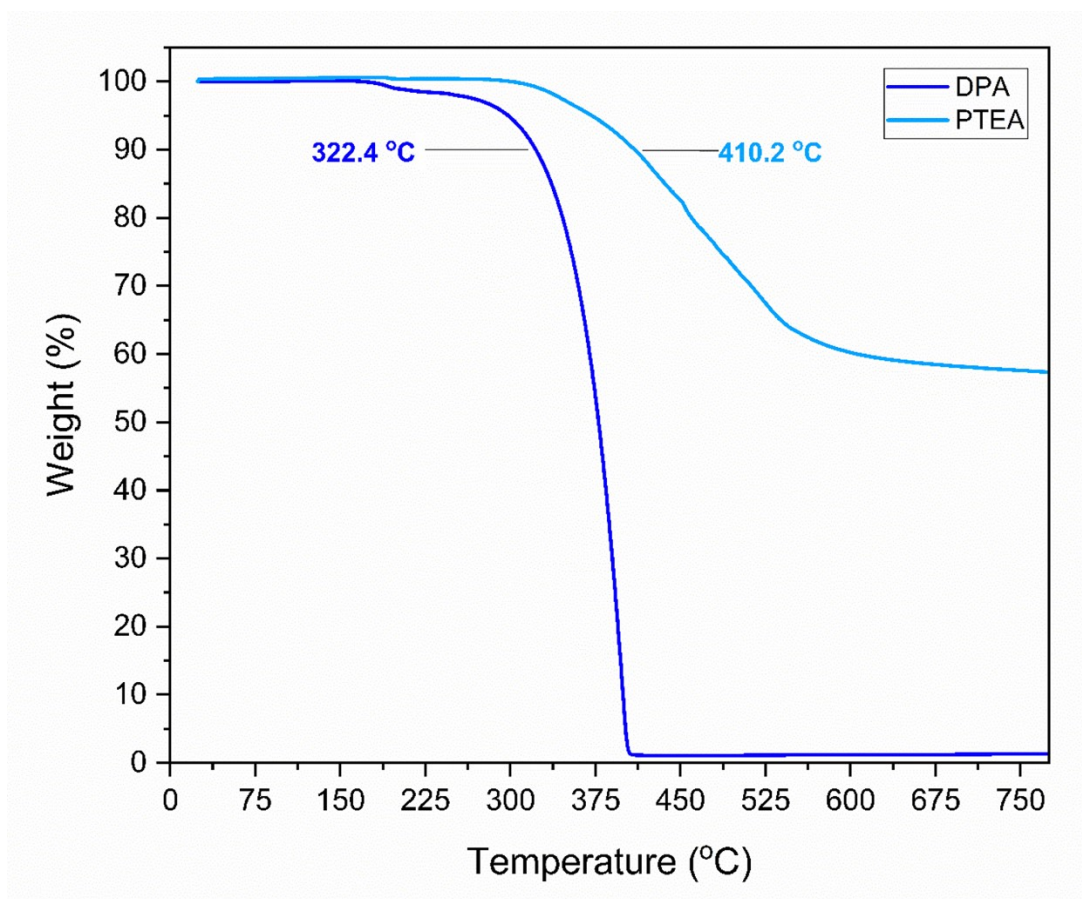


Figure S8. Thermogravimetric analysis (TGA) of DPA and PTEA to compare degradation temperature (10% mass loss). DPA 10% mass loss at 322 °C, PTEA 10% mass loss at 410 °C.

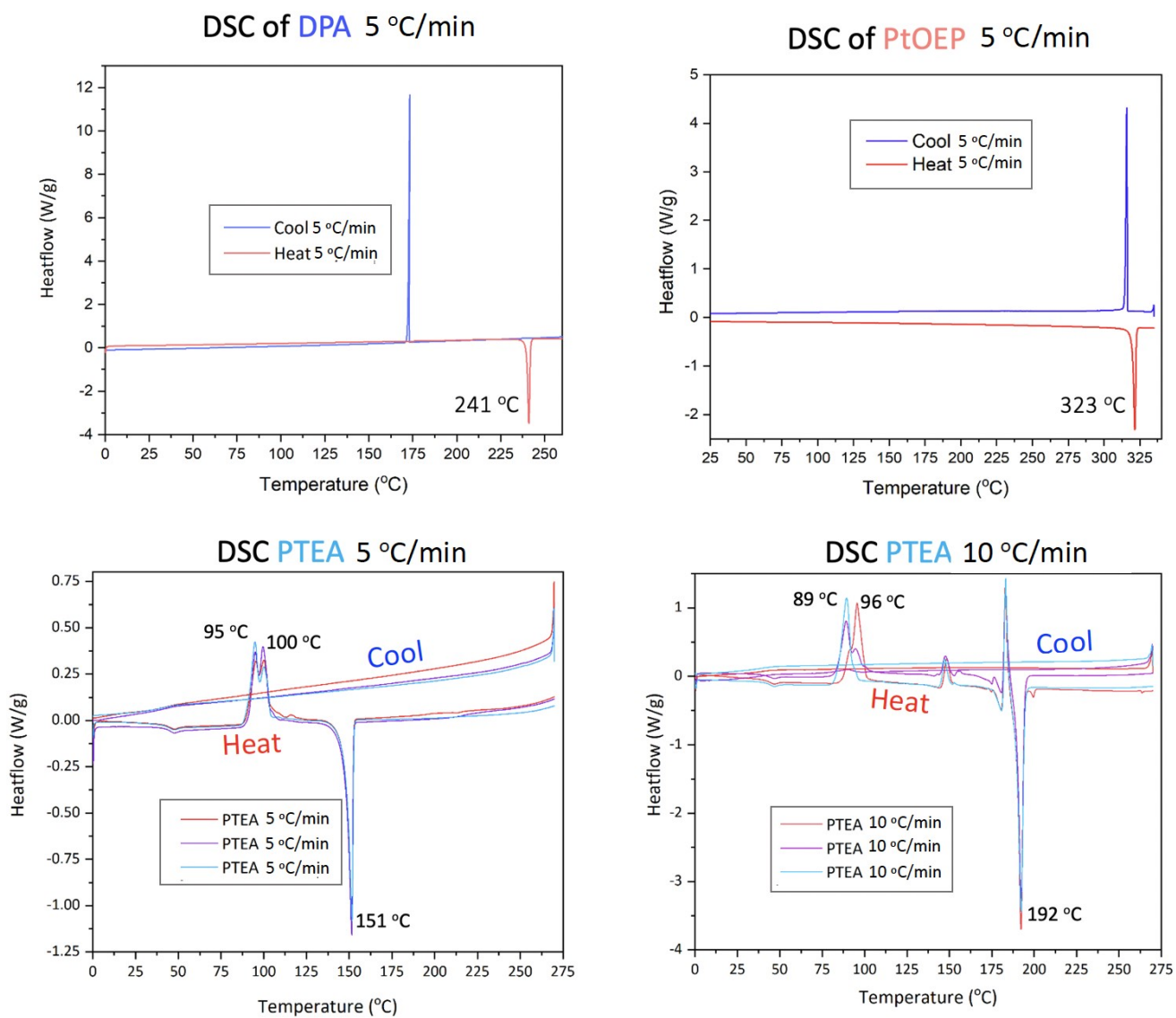


Figure S9. Differential scanning calorimetry (DSC) of DPA, PtOEP, and PTEA at various ramp rates detailed in graph title (°C/minute). First cool and second heat at identical ramp rates for all respective scans. First heat has been removed. All DSC curves are “exo up.”

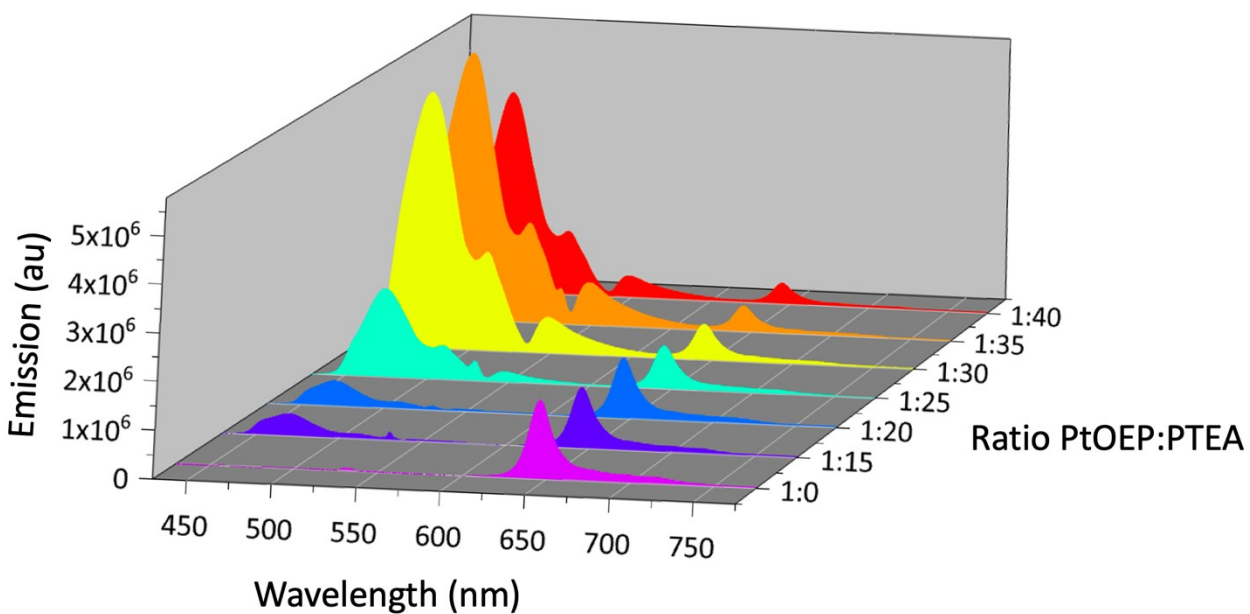


Figure S10. Emission spectrum as a function of ratio of PtOEP (excited species) and PTEA (quencher species) in THF. Excitation at 532 nm. PtOEP maximum emission at 645 nm. PTEA maximum emission 470 nm. x axis = wavelength, y axis = emission intensity (a.u.), z axis = ratio of PtOEP:PTEA. (0.1 mg PtOEP: “ x ” mg PTEA in 3.5 mL THF).

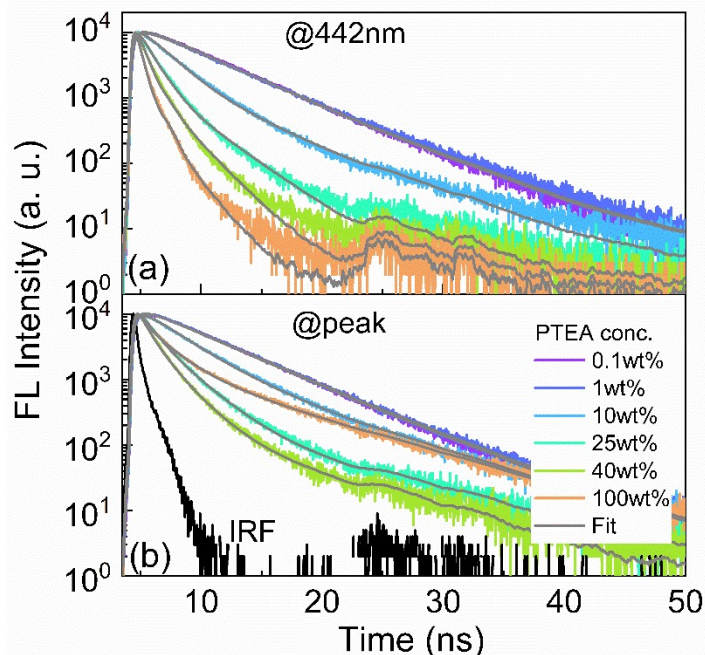


Figure S11. Fluorescence transients as a function of increasing PTEA concentration in PMMA matrix (drop-cast films) Excitation wavelength: 375 nm. (a) Measured at 442 nm and (b) measured at FL peak maximum. See **Table S2** for fitting parameters.

Table S2: Fitting parameters of FL transients of drop-cast PTEA/PMMA films.

PTEA conc. in PMMA	τ_1 ns	f_1	τ_2 ns	f_2	τ_3 ns	f_3	$\langle\tau\rangle$ ns
Measured at 442 nm							
0.1wt%	--	--	--	--	5.28	100	5.28*
1wt%	--	--	--	--	5.41	100	5.41*
10wt%	--	--	1.95	62	5.57	38	3.33
25wt%	--	--	0.86	67	3.32	33	1.67
40wt%	--	--	0.51	72	2.3	28	1.01
100wt%	--	--	0.29	87	1.88	13	0.50
Measured at FL peak maximum							
0.1wt%	--	--	--	--	5.41	100	5.41*
1wt%	--	--	--	--	5.52	100	5.52*
10wt%	--	--	2.91	63	7.14	37	4.48
25wt%	0.76	33	2.48	57	8.56	10	2.52
40wt%	0.58	41	1.96	49	7.07	10	1.91
100wt%	0.49	20	2.15	39	7.80	41	4.13

f_i – fractional intensity, τ_i – FL lifetime, $\langle\tau\rangle$ – singlet exciton lifetime calculated as $\langle\tau\rangle = \sum f_i \cdot \tau_i$. * - monoexponential FL decay constant ($\langle\tau\rangle = \tau$).

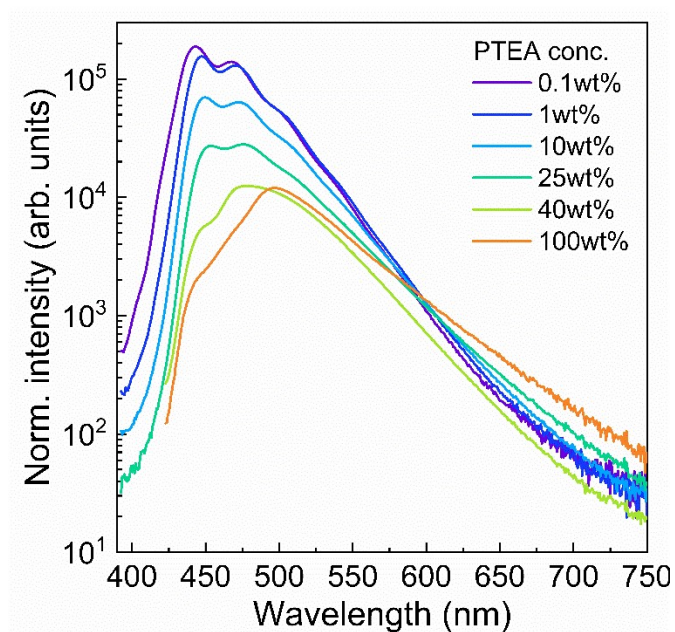


Figure S12. Absorbance corrected FL spectra of PTEA doped PMMA films. Excitation at 375 nm.

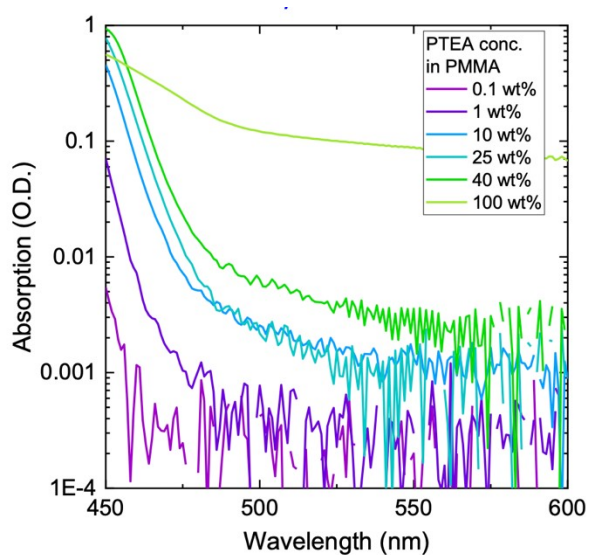


Figure S13. Absorption spectra of DPA-free PMMA films doped with increasing concentration of PTEA (indicated).

Optical Microscopy Data

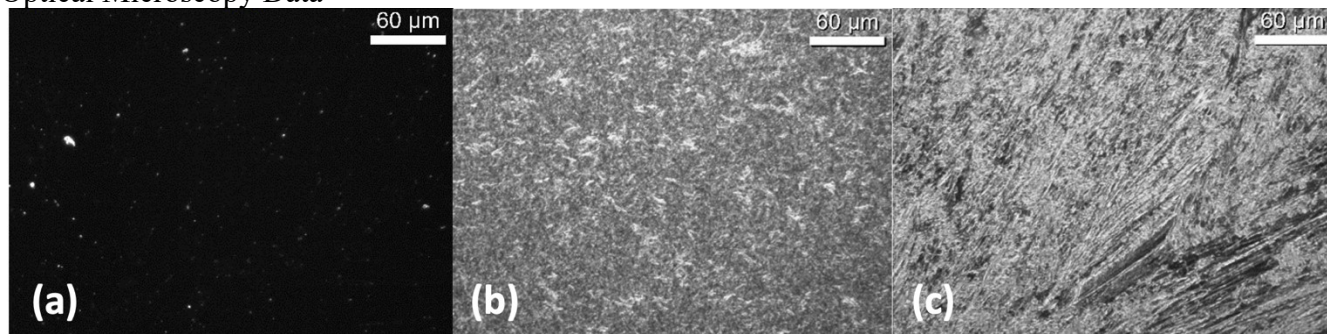


Figure S14. Microscope images of (a) 25 wt% PTEA and (b) 40 wt% PTEA doped into PMMA. (c) Neat PMMA. Images obtained with an Olympus BX-51 microscope working in dark field mode.

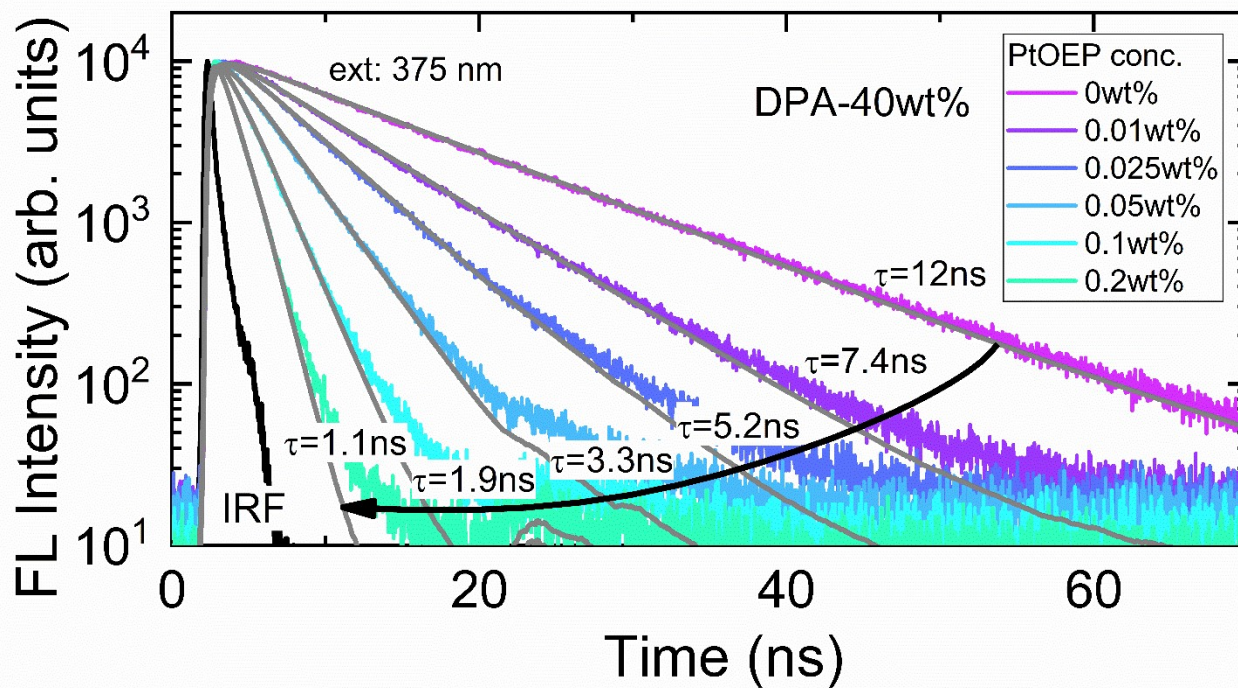


Figure S15. FL transients of sink-free UC films (40 wt% DPA) with varying PtOEP concentration (indicated). Excitation wavelength: 375 nm. Transients recorded at 436 nm. IRF – instrument response function.

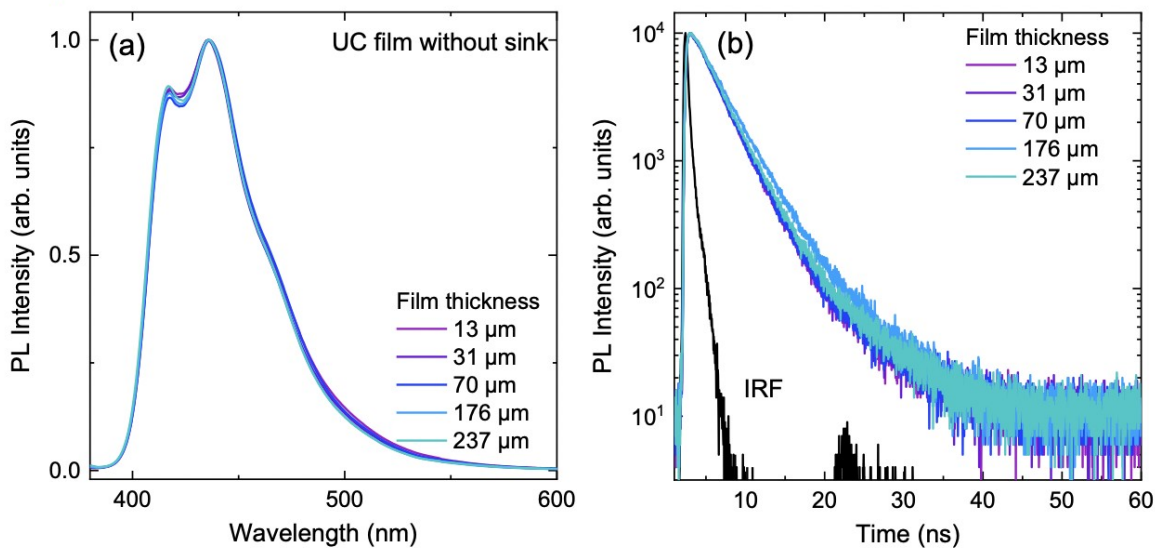


Figure S16. (a) Normalized FL spectra and (b) transients of sink-free UC films (40 wt% DPA, 0.05 wt% PtOEP) with varying thicknesses (indicated). Excitation wavelength: 375 nm. Transients recorded at 436 nm. IRF – instrument response function.

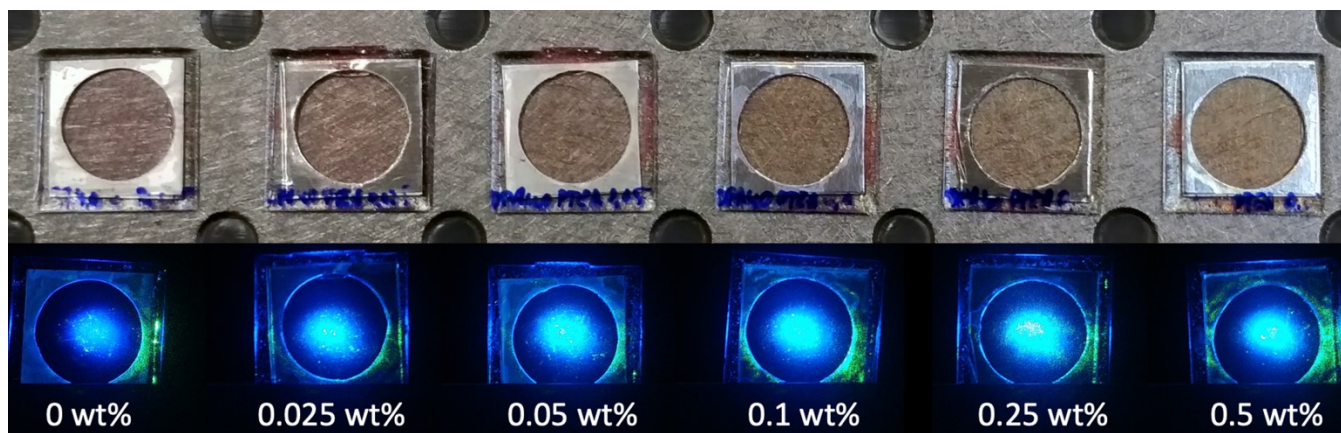


Figure S17. Photos of six melt-processed PMMA films (PtOEP = 0.05 wt%, DPA = 40 wt%) with increasing PTEA content (indicated). Photos were taken under identical camera settings and excitation exposure at 532 nm.

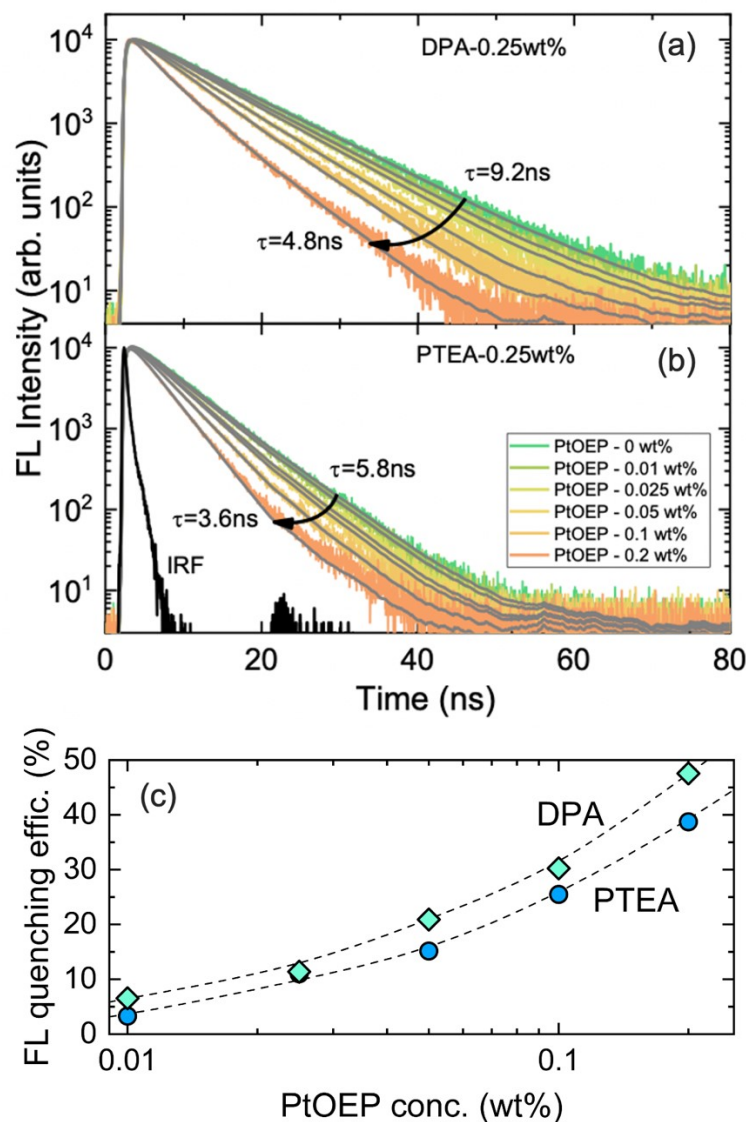


Figure S18. FL transients of 0.25 wt% DPA (a) and 0.25 wt% PTEA (b) in PMMA films as a function of increasing PtOEP concentration. Excitation wavelength = 375 nm. Transients measured at emission maxima (407 nm for DPA and 446 nm for PTEA). IRF – instrument response function. Grey lines are mono-exponential fits. (c) FL quenching efficiency, calculated according to

$$\text{Quenching efficiency} = 1 - \frac{\tau_{w/PtOEP}}{\tau_{w/o PtOEP}}$$

where $\tau_{w/PtOEP}$ is FL lifetime with PtOEP and $\tau_{w/o PtOEP}$ is fluorescence lifetime without PtOEP. Despite similar quenching trends observed for both DPA- and PTEA-containing film sets upon increasing PtOEP concentration, DPA exhibited somewhat stronger overall quenching by PtOEP compared to PTEA (Figure S18c). Stern-Volmer quenching analysis yielded Stern-Volmer constants (K_{SV}) of $2.8 \cdot 10^2 \text{ M}^{-1}$ and $2.0 \cdot 10^2 \text{ M}^{-1}$ for 0.25 wt% DPA and 0.25 wt% PTEA, respectively.

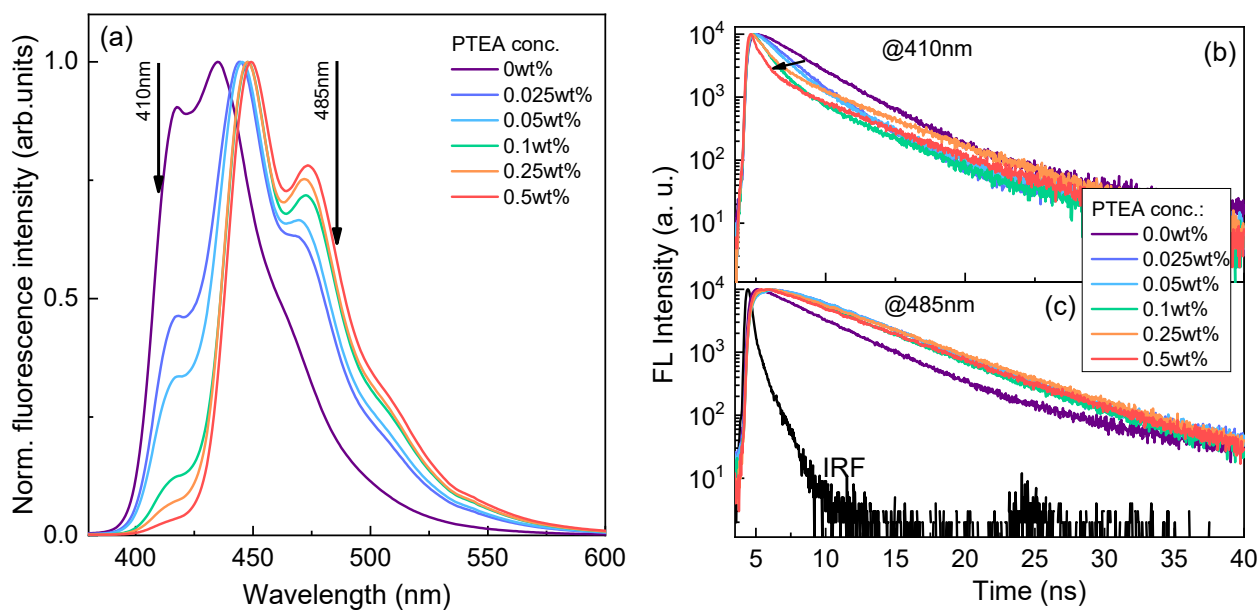


Figure S19. FL spectra (a) and transients of UC films measured at 410 nm (b) and 485 nm (c) as a function of singlet sink PTEA concentration. Excitation wavelength – 375 nm. IRF – instrument response function. See **Table S2** for fitting parameters and calculated energy transfer efficiency versus PTEA concentration in UC films.

Table S3. Fitting parameters of Fl transients of UC films and energy transfer efficiency. See **Figure S9** and **Figure 7** for plots.

PTEA conc. in UC film	410 nm					485 nm
	τ_1 ns	f_1	τ_2 ns	f_2	ϕ_{ET} %	τ ns
0.0wt%	3.22	100	--	--	0	3.83
0.025wt%	1.96	81	5.44	19	39	4.64
0.05wt%	1.52	66	4.84	34	53	4.79
0.1wt%	0.82	57	4.42	43	75	4.80
0.25wt%	0.68	37	4.89	63	79	5.37
0.5wt%	0.37	40	4.76	60	89	5.24

ϕ_{ET} - energy transfer efficiency from DPA to PTEA calculated from the accelerated decay component of DPA.

$$\phi_{ET} = 1 - \tau_{(DPA+PTEA)} / \tau_{DPA}$$

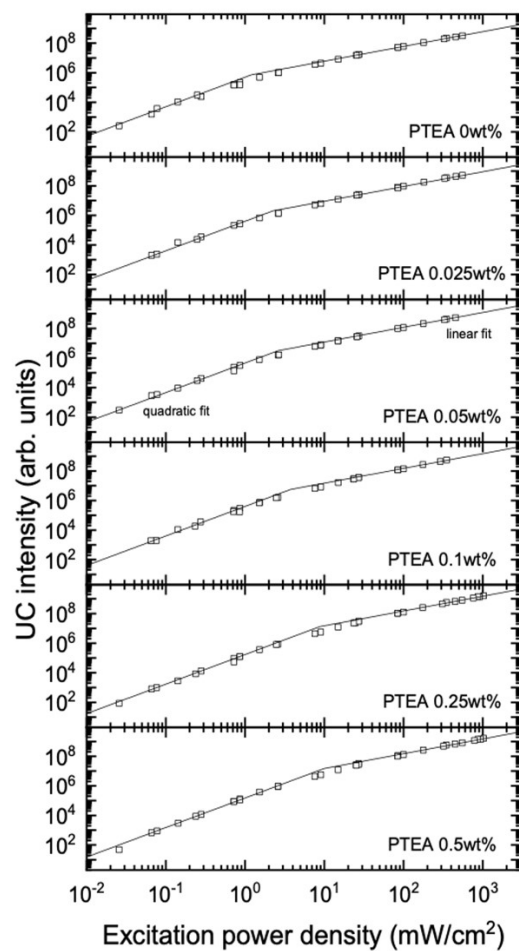


Figure S20. UC intensity dependence on excitation power density. See **Figure 8** for determined UC threshold at increasing PTEA concentrations in PMMA films.

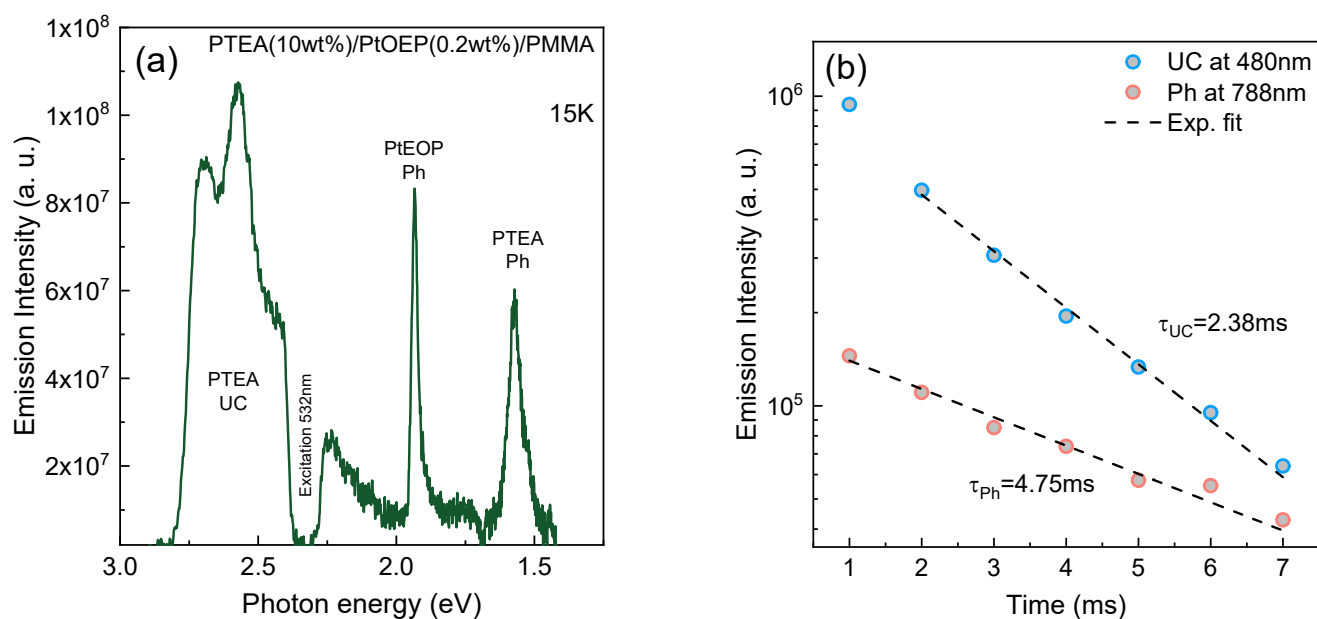


Figure S21. (a) The emission spectrum of PTEA (10 wt%)/PtOEP (0.2 wt%)/PMMA films, allowing for determination of the triplet energy level of PTEA, studying PAH phosphorescence at low temperatures (15 K). (b) The emission decay measured at 480 nm (within PTEA S_1 level) and 788 nm (within PTEA T_1 level). T_1 of PTEA (first vibronic peak) = 1.57 eV (T_1 of DPA = 1.72 eV), S_1 of PTEA = 2.70 eV. Emission transients of UC and Ph bands of PTEA with corresponding lifetimes indicated. The relation $\tau_{Ph} = 2 \times \tau_{UC}$ confirms that the emission band at 788 nm originates from the T_1 of PTEA.