

## Supplementary Information

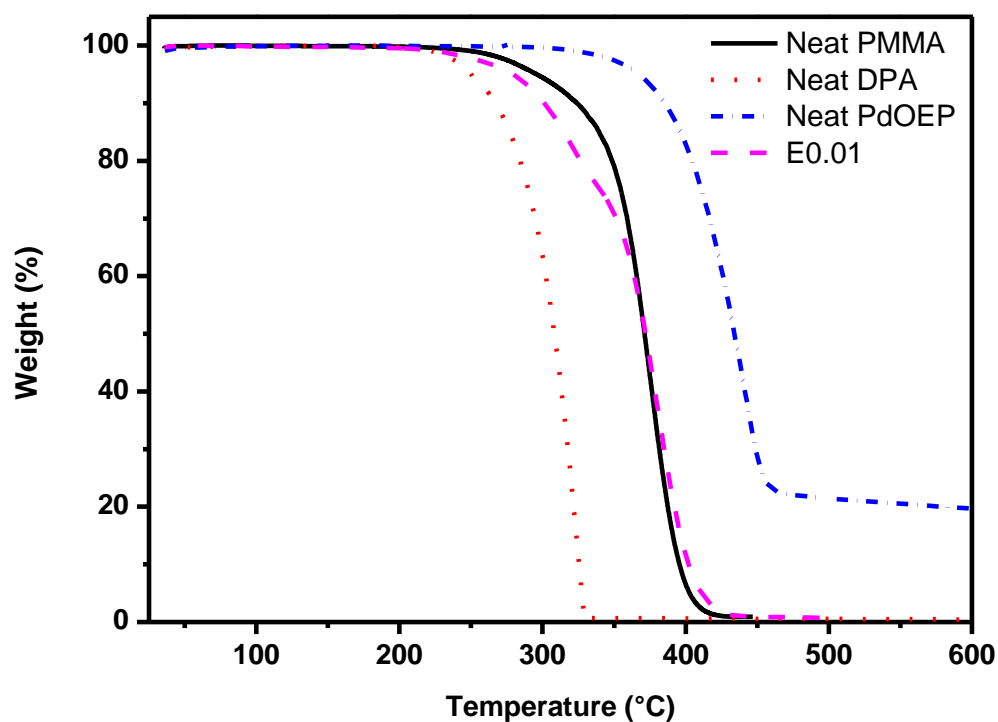
# Melt-processed polymer glasses for low-power upconversion via sensitized triplet-triplet annihilation

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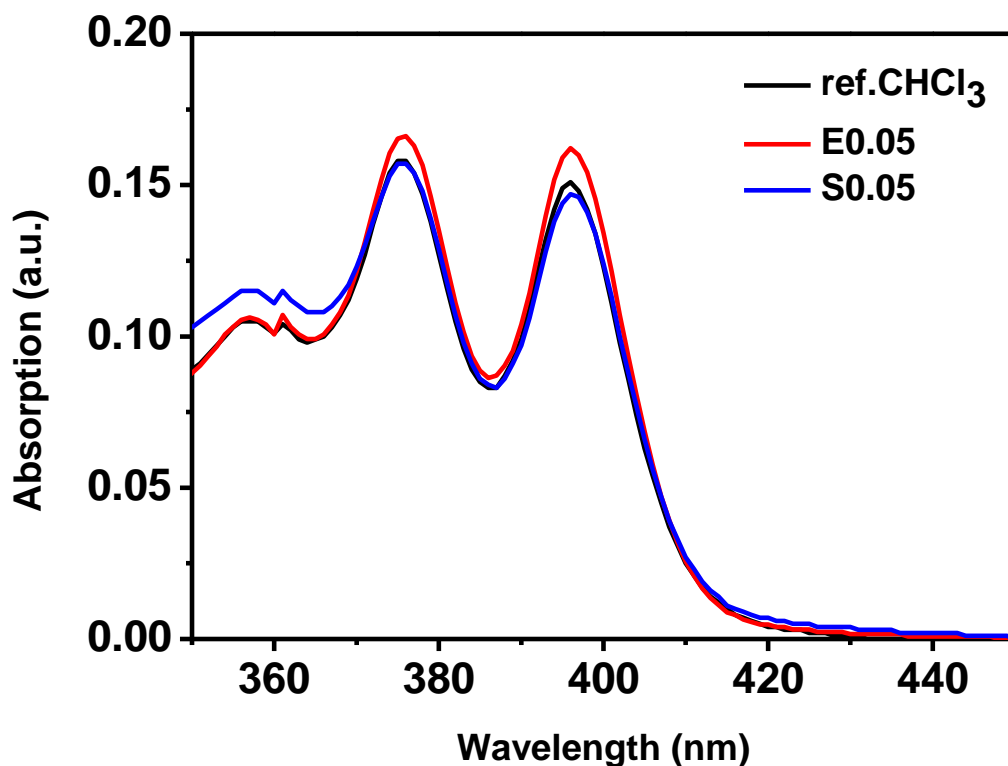
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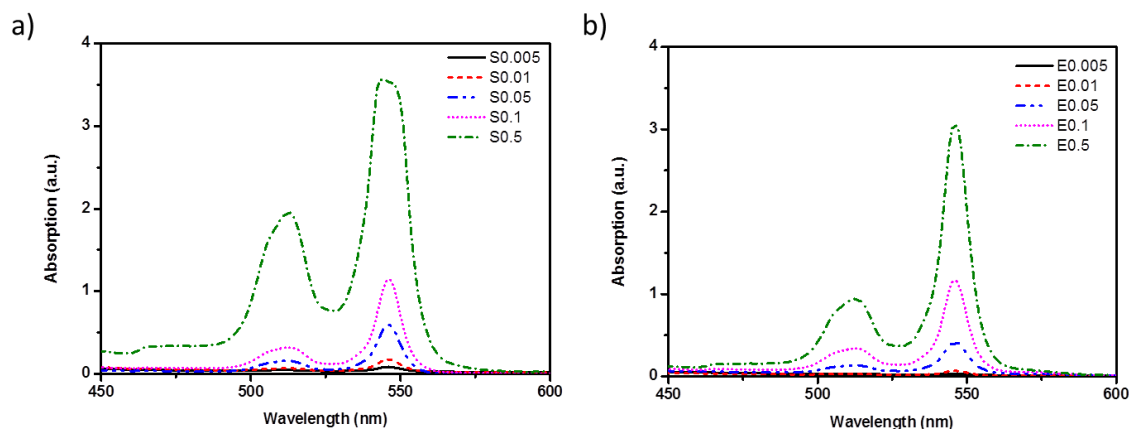
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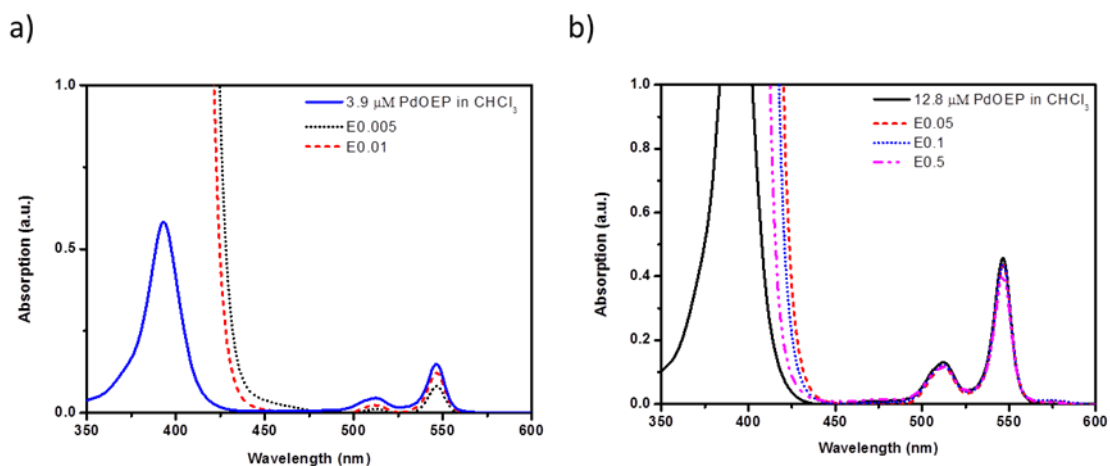
**Fig. S1** Thermogravimetric analysis (TGA) traces of neat PMMA, neat DPA, neat PdOEP, and blends melt-processed at 240 °C, comprising 0.01% w/w PdOEP and 25% w/w DPA, all recorded in air.



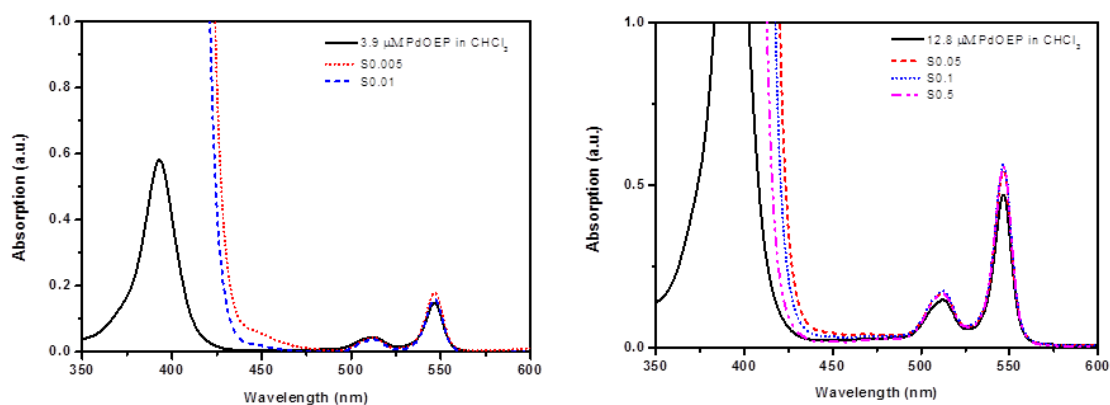
**Fig. S2** Absorption spectra of DPA in E0.05 and S0.05 (6.4 mg of film dissolved with 19 mL of CHCl<sub>3</sub>) compared to a reference solution of DPA dissolved in CHCl<sub>3</sub> (0.09 mM).



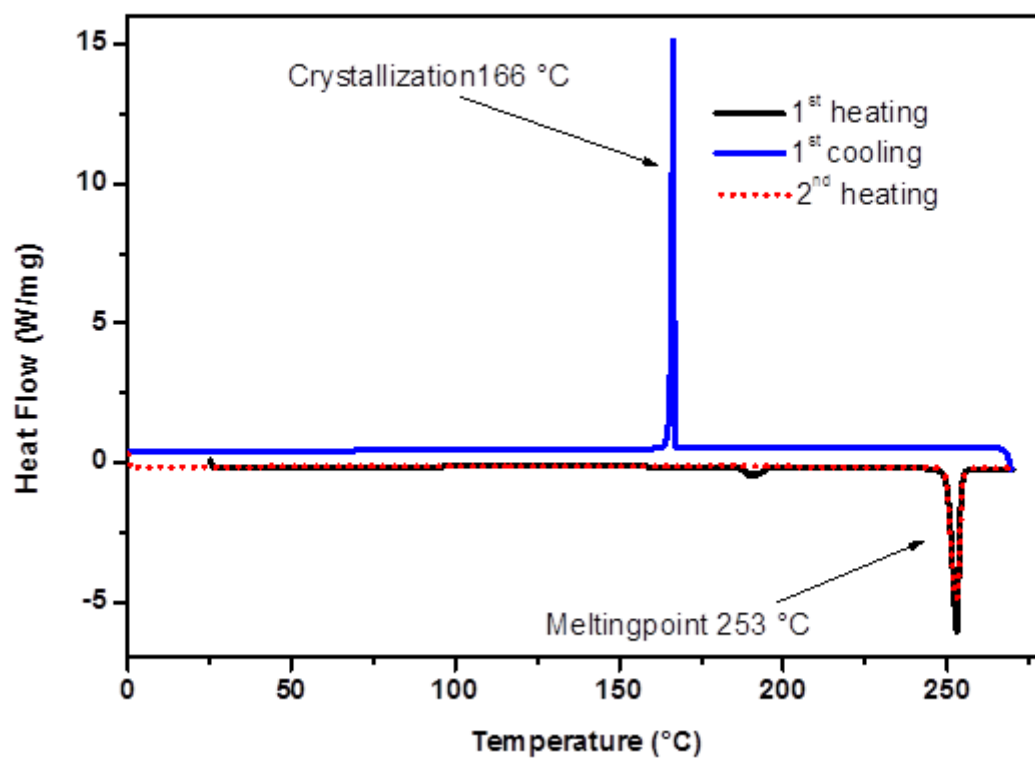
**Fig. S3** Absorption spectra of PMMA films: a) Series S by co-precipitation from DMF; b) Series E premixed by melt-compounding In a twin-screw extruder. The DPA content was kept constant at 25 % w/w and the concentration of PdOEP was 0.005%, 0.01%, 0.05%, 0.1% and 0.5% w/w relative to the amount of to PMMA. Thickness of films were varied from 140 to 200  $\mu\text{m}$ .



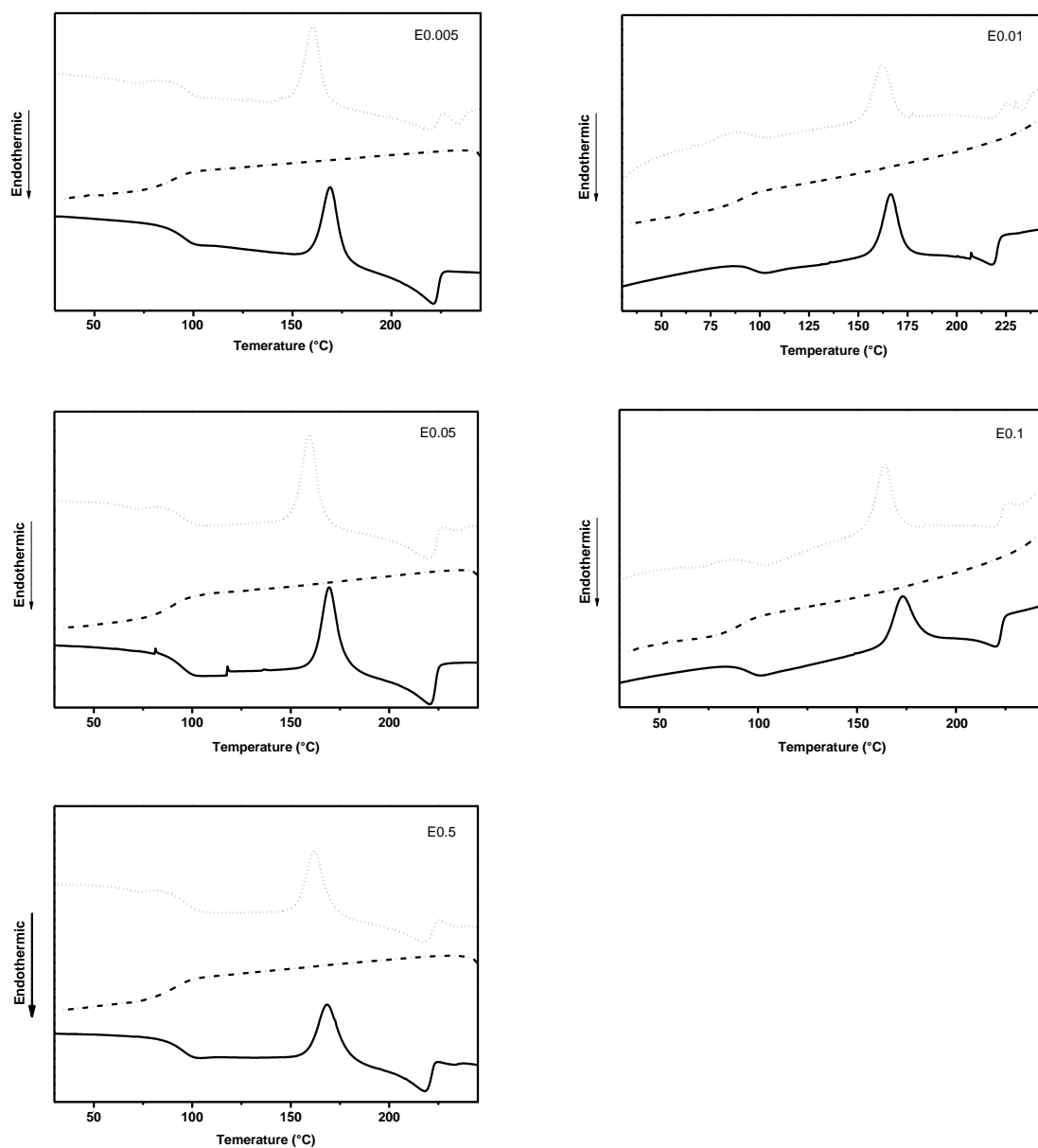
**Fig. S4** Absorption spectra of series E a) 250 mg of E0.005 and 125 mg of E0.01 were separately dissolved in 4 mL of  $\text{CHCl}_3$ . As reference, a  $3.9 \mu\text{M}$  solution of PdOEP in  $\text{CHCl}_3$  was measured. b) 200 mg of E0.05, 100 mg of E0.1, and 20 mg of E0.5 were separately dissolved in 10 mL of  $\text{CHCl}_3$ . As reference, a  $12.8 \mu\text{M}$  solution of PdOEP in  $\text{CHCl}_3$  was measured.



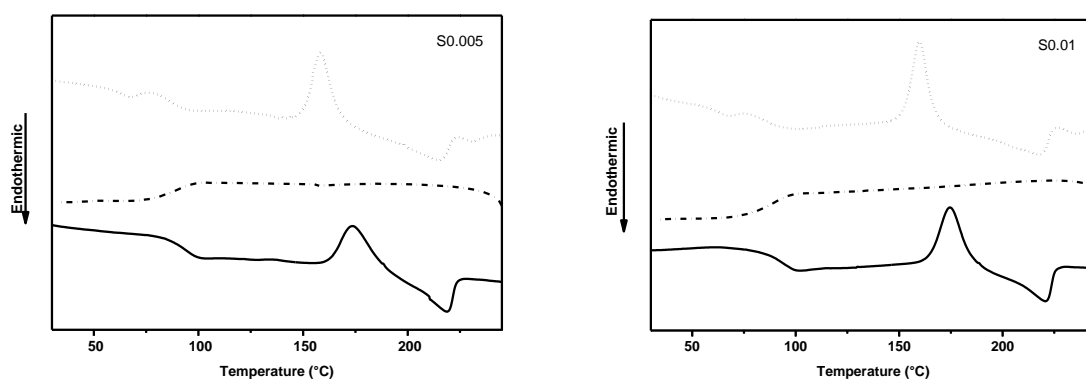
**Fig. S5** Absorption spectra of series S a) 250 mg of S0.005 and 125 mg of S0.01 were separately dissolved in 4 mL of  $\text{CHCl}_3$ . As reference, a  $3.9 \mu\text{M}$  solution of PdOEP in  $\text{CHCl}_3$  was measured. b) 200 mg of S0.05, 100 mg of S0.1, and 20 mg of S0.5 were separately dissolved in 10 mL of  $\text{CHCl}_3$ . As reference, a  $12.8 \mu\text{M}$  solution of PdOEP in  $\text{CHCl}_3$  was measured.

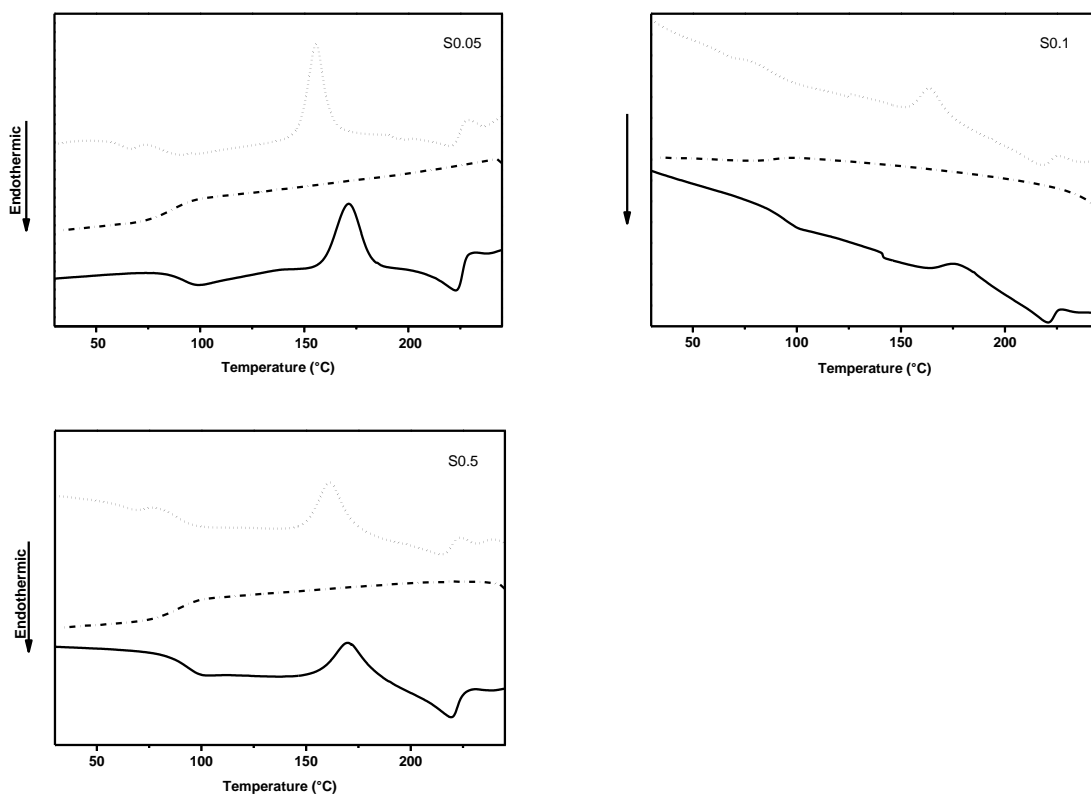


**Fig. S6** Differential scanning calorimetry (DSC) traces of neat DPA, first heated from 25 °C to 260 °C then cooled to 0 °C and heated again to 260 °C, recorded under nitrogen.

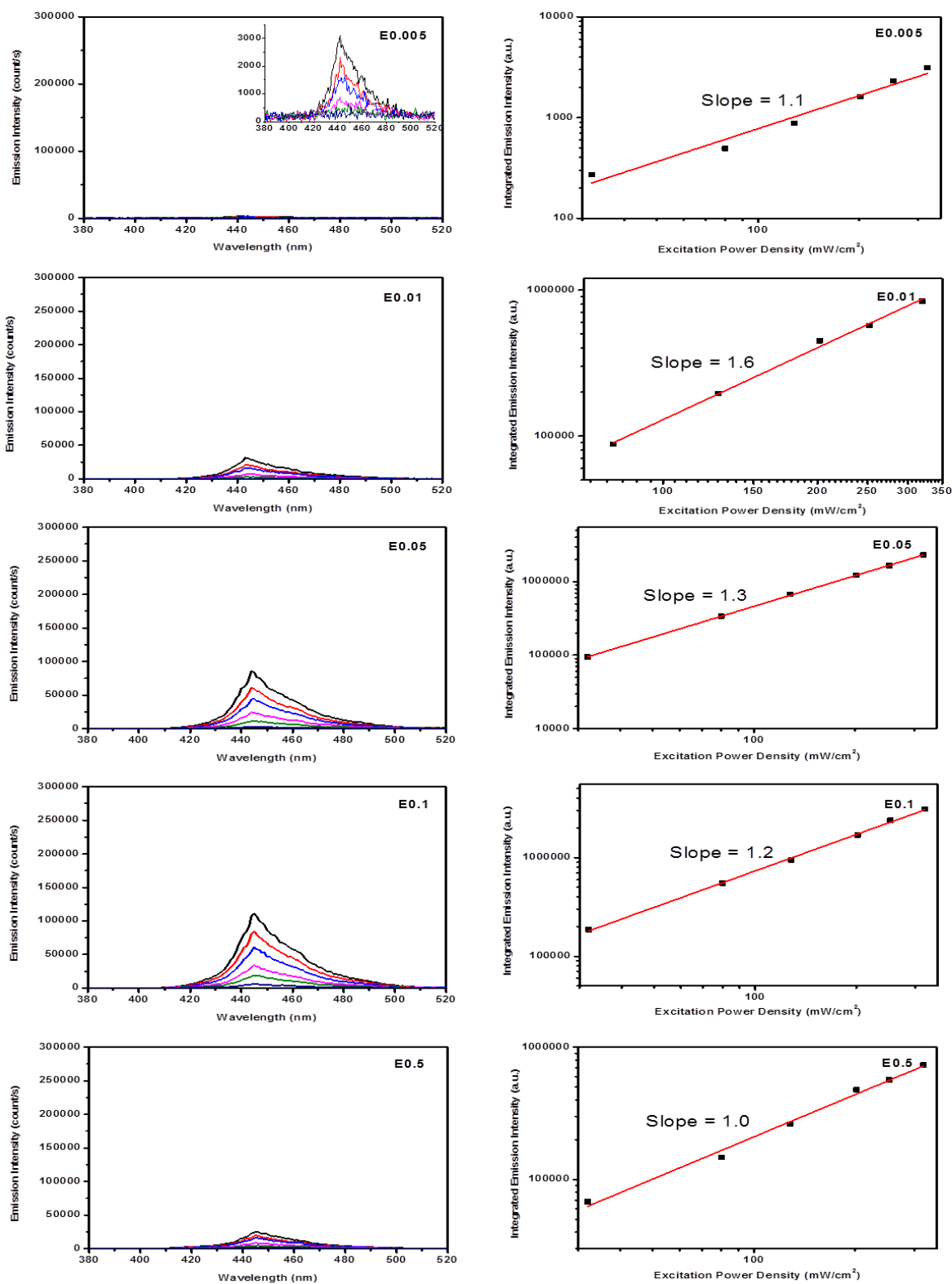


**Fig. S7** Differential scanning calorimetry (DSC) traces of all series E samples, recorded under nitrogen. Samples were first heated from 25 °C to 250 °C (····), cooling from 250 °C to 0 °C (---), and heated again from 0 °C to 260 °C (—). All with heating or cooling rates of 10 °C/min.

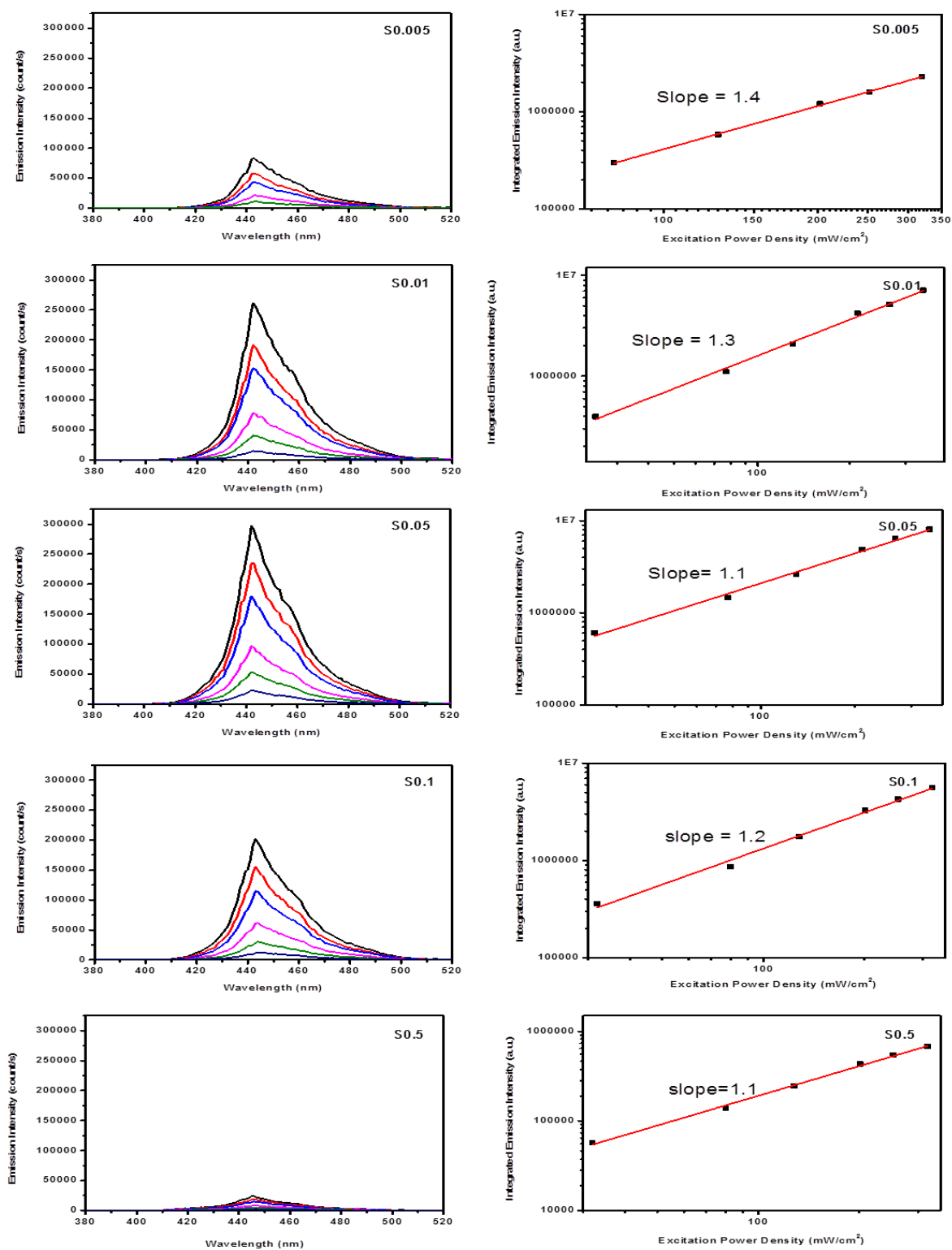




**Fig. S8** Differential scanning calorimetry (DSC) traces of all series S samples, recorded under nitrogen. Samples were first heated from 25 °C to 250 °C(⋯), cooled from 250 °C to 0 °C(---), and heated again from 0 °C to 260 °C(—) under N<sub>2</sub> atmosphere. All with heating or cooling rates of 10 °C/min.

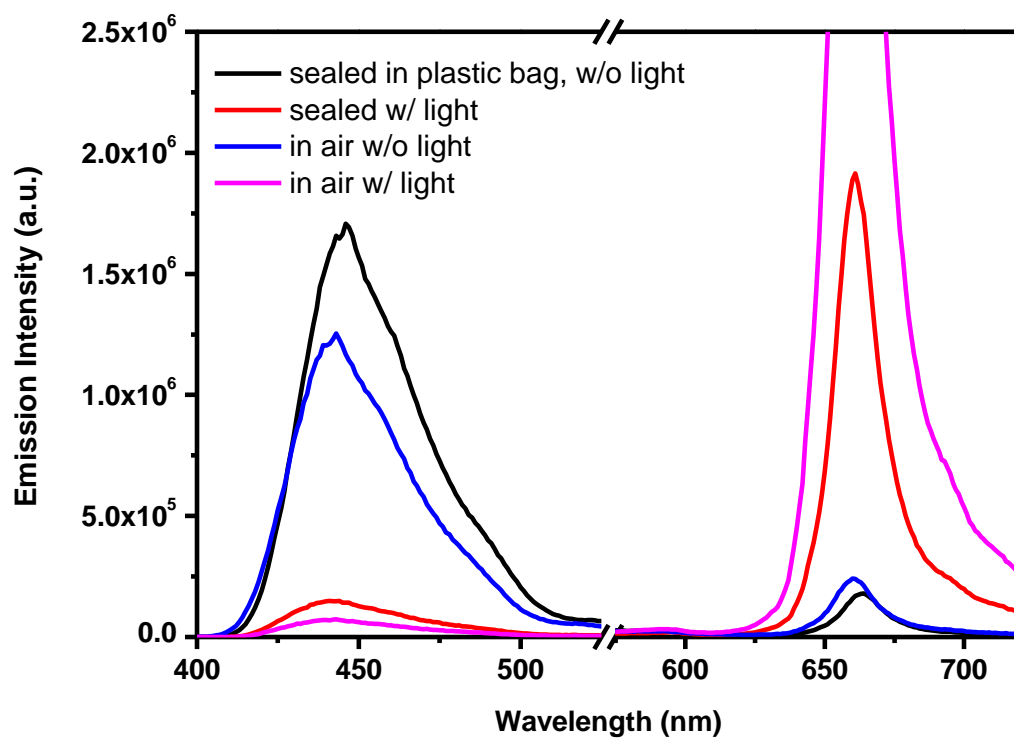


**Fig. S9** Upconverted emission spectra of Series E excited with HeNe laser at 543nm with variation of excitation power density from 34 mW/cm<sup>2</sup> to 340 mW/cm<sup>2</sup>.

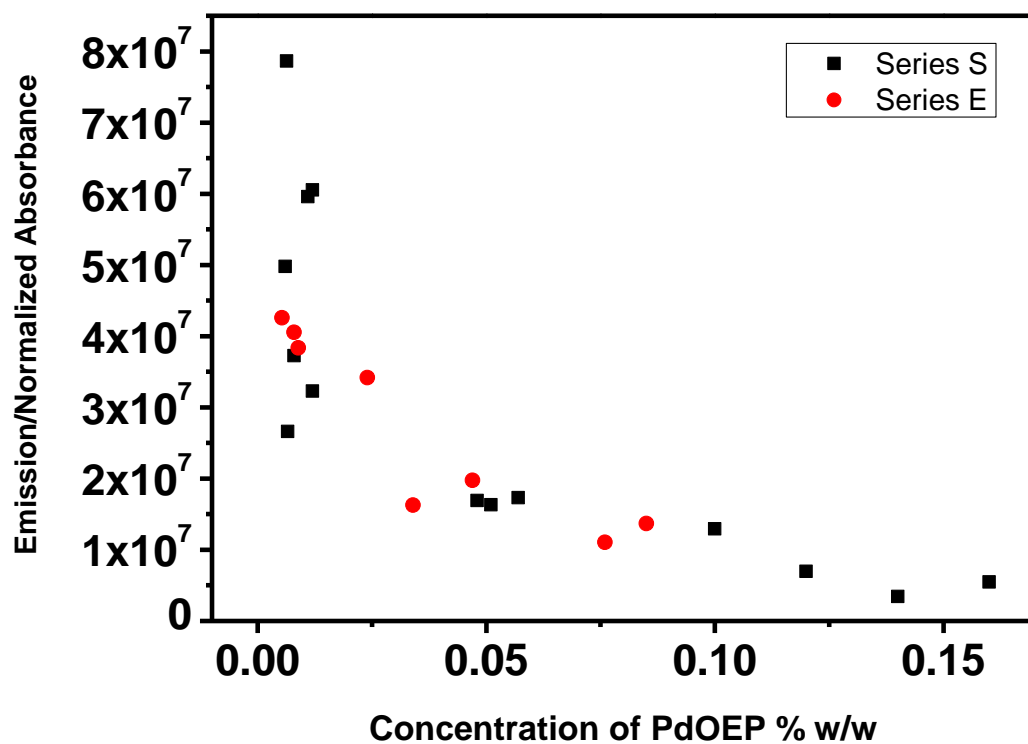


**Fig. S10** Upconverted emission spectra of Series S excited with HeNe laser at 543nm with variation of excitation power density from 34 mW/cm<sup>2</sup> to 340 mW/cm<sup>2</sup>.





**Fig. S11** Upconverted fluorescence and phosphorescence decay of E0.05 films stored under different condition of light and atmospheres.



**Fig. 12** Integrated upconverted emission intensity normalized by the absorbance of the films of series E and S films as a function of PdOEP concentration (experimentally determined value, not nominal concentration). The excitation power density at 543 nm was fixed at  $340 \text{ mw/cm}^2$ .

Series S	nominal PdOEP %	Absorption (a.u.)	Thickness (cm)	[C] (M)	v (mm <sup>3</sup> )	m (mg)	mass total (mg)	Experimental PdOEP %
Films	0.005	0.044	0.012	1.04297E-04	27	0.001783	28.795	0.008
	0.01	0.104	0.017	1.74014E-04	38.25	0.004213	49.764	0.011
	0.05	0.399	0.013	8.73032E-04	29.25	0.016164	34.076	0.059
solution	0.005	0.031	1	8.81784E-07	3000	0.001675	28.795	0.007
	0.01	0.082	1	2.33246E-06	2600	0.003839	49.764	0.010
	0.05	0.321	1	9.13073E-06	2600	0.015027	34.076	0.055

Table S1, exact concentration of PdOEP of a series S from S0.005 to S0.05 measured in solid state and in solution.

Calculation of PdOEP concentration of films from absorption bands of PMMA films.

For example sample S0.01, we measured directly its absorption in solid state with a Shimadzu UV-2401PC UV-vis spectrophotometer  $A = 0.085$ , its thickness = 0.12 mm, and the weight of cut film with dimension 25mm × 9mm × 0.12 mm = 35.34 mg.

The absorption of PdOEP in chloroform allowed to calculate the extinction coefficient of PdOEP. And as absorption of the PdOEP solution = 0.45 with concentration of PdOEP in chloroform = 12.8 μM and According to Beer Lambert's Law  $A = \epsilon[C]l$

$$\epsilon_{\text{PdOEP}} = \frac{0.45}{12.8 \times 10^{-6}} = 35156 \text{ cm}^{-1} \text{M}^{-1}$$

So the concentration [C] of PdOEP is:

$$[C] = \frac{A}{\epsilon l} = \frac{0.085}{35156 \times 0.012} = 0.0002 \text{ M}$$

The exact mass of PdOEP experimentally obtained ( $m_{\text{exp}}$ ) in PMMA:  $m_{\text{exp}} = [C] \times M(\text{PdOEP}) \times V$

With  $M(\text{PdOEP}) = 633 \text{ g/mol}$  and  $V = 25 \times 9 \times 0.12 = 27 \text{ mm}^3$

$$m_{\text{exp}} = 0.0002 \times 633 \times 27 \times 10^{-6} = 3.4 \times 10^{-6} \text{ g}$$

As nominal mass of S0.01 =  $2.8 \times 10^{-6} \text{ g}$

Exact % of PdOEP of film S0.01 = 0.011 %