Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information for

Thiol-ene Click Chemistry : A Modular Approach to Solid-State Triplet-Triplet Annihilation Upconversion

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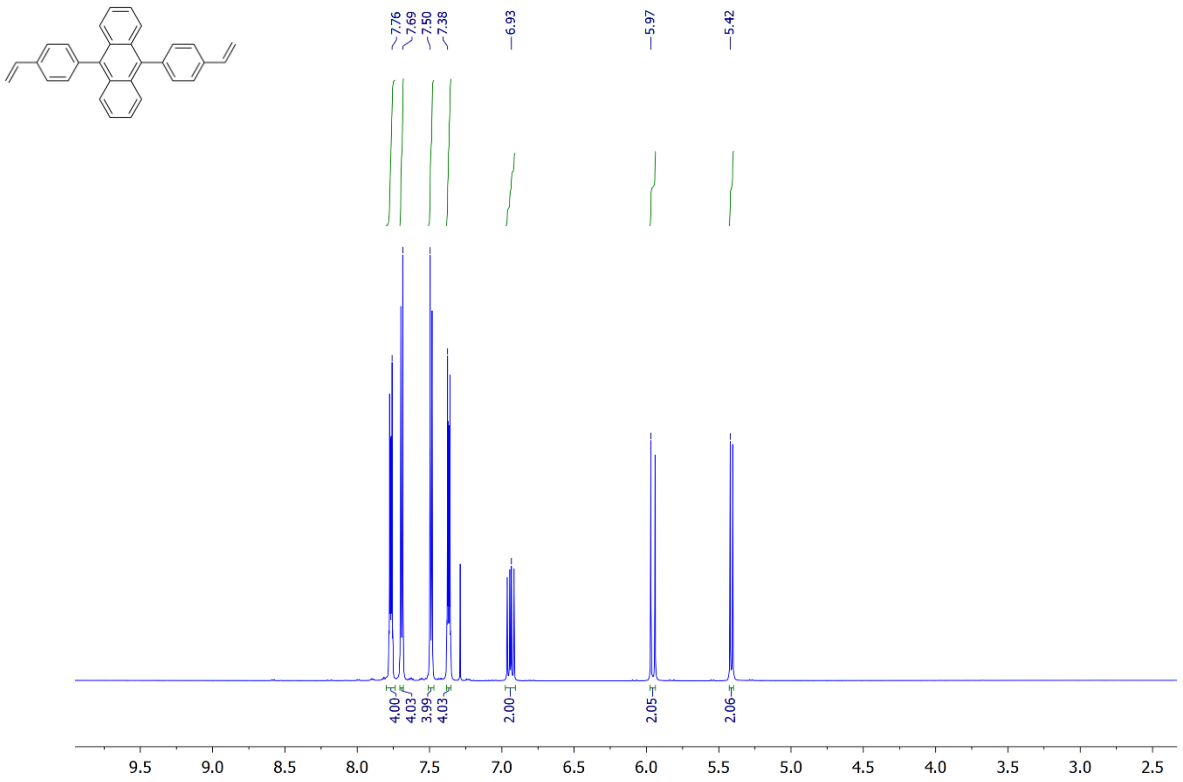

Figure S1. ^{1}H NMR ($CDCl_3$, 600 MHz) spectra of **1**.

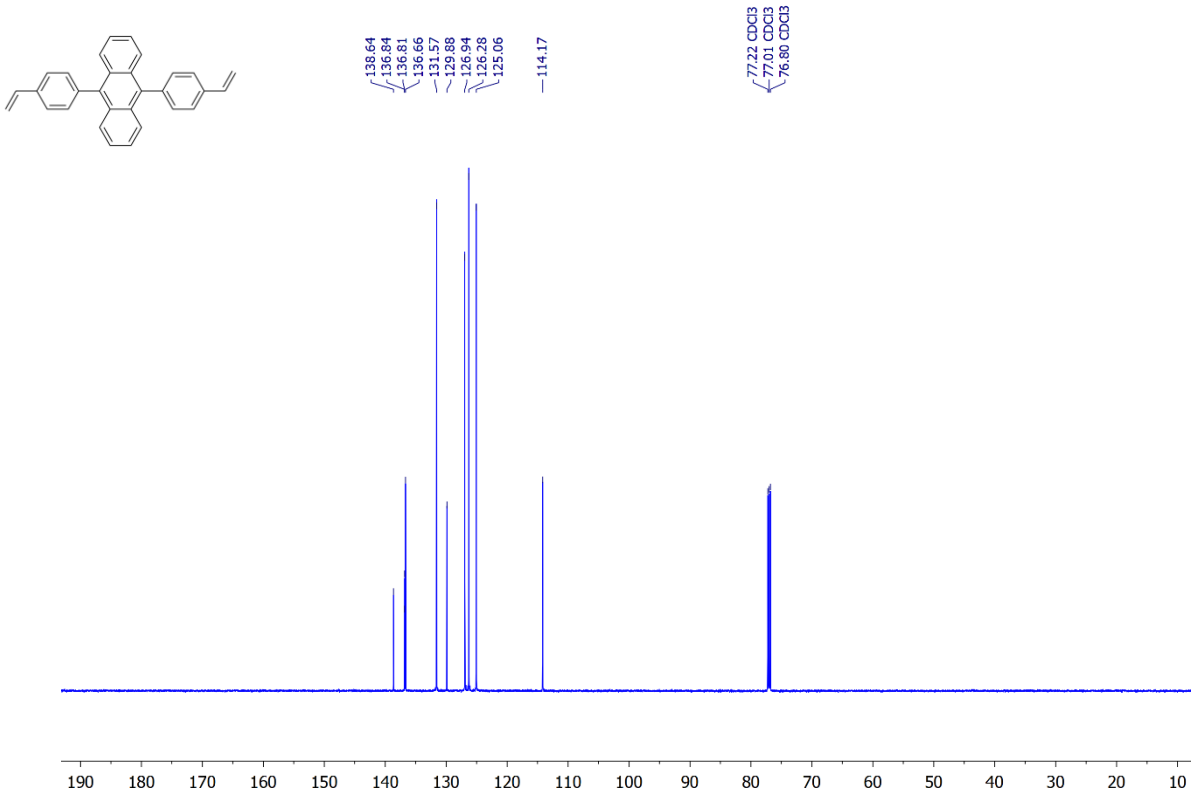

Figure S2. ^{13}C NMR ($CDCl_3$, 151 MHz) spectra of **1**.

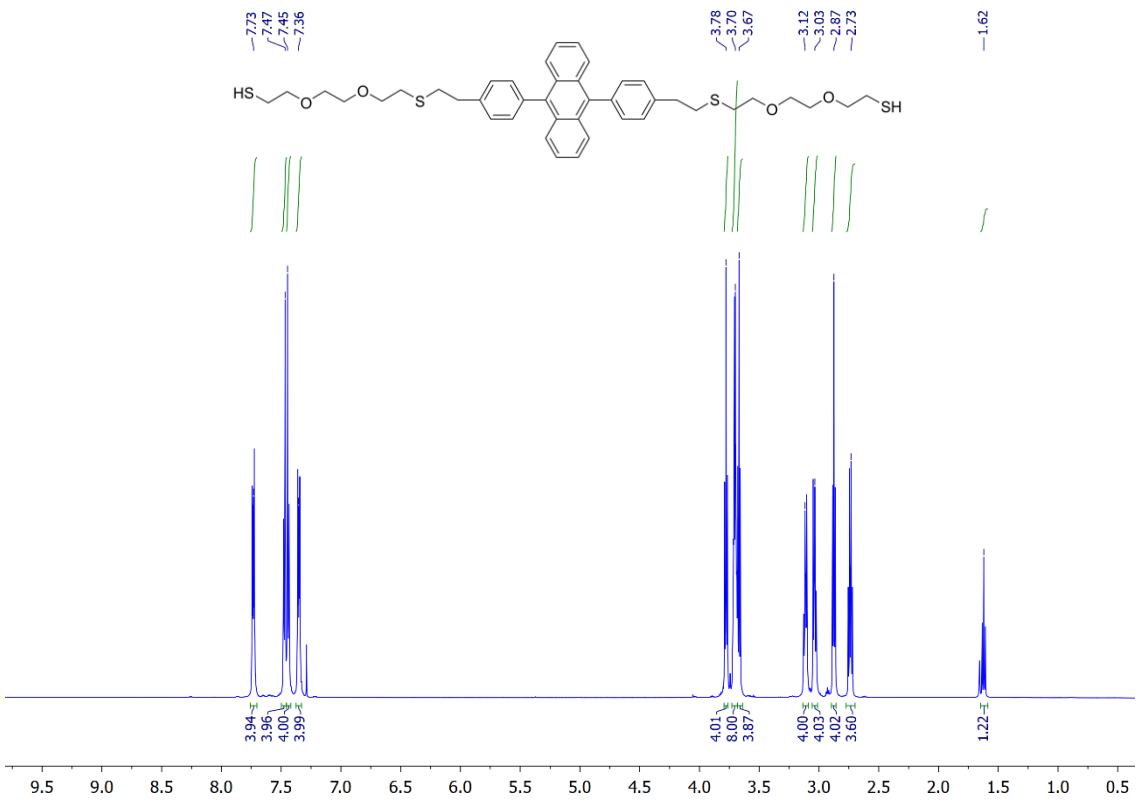

Figure S3. ^{1}H NMR ($CDCl_3$, 600 MHz) spectra of **2**.

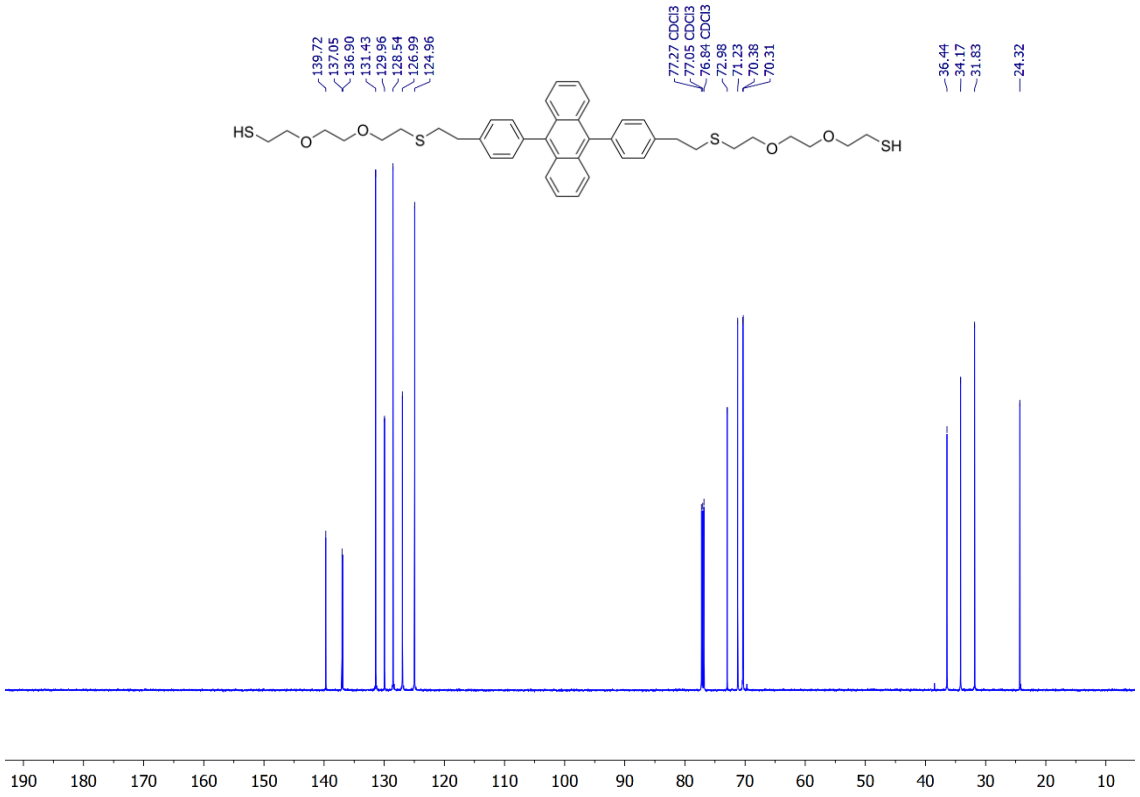

Figure S4. ^{13}C NMR ($CDCl_3$, 151 MHz) spectra of **2**.

Optical Characterization of Functionalized and Unmodified DPA

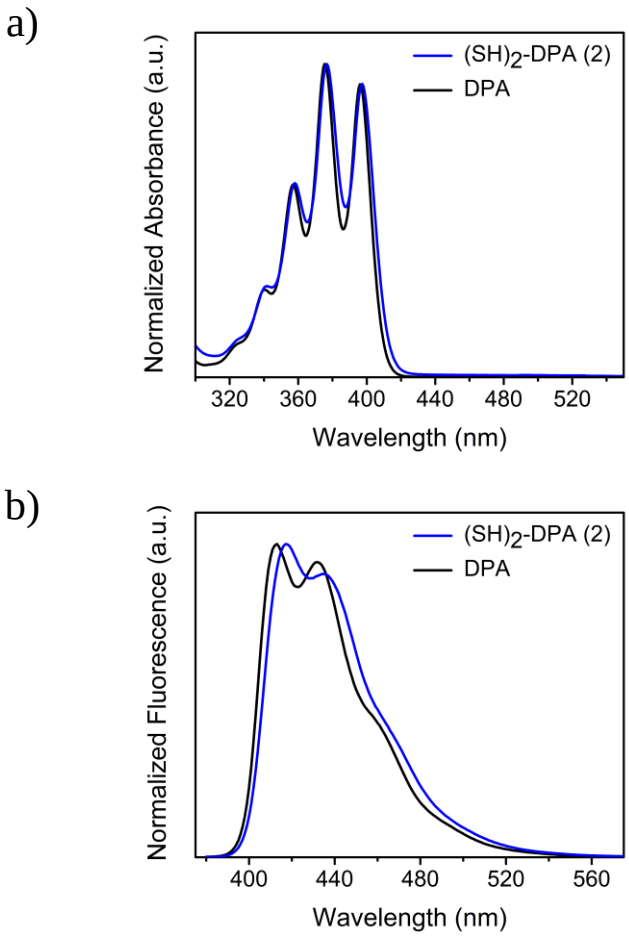

Figure S5. Absorbance (a) and fluorescence (b) spectra of the thiol functionalized DPA derivative (**2**) and unmodified 9,10-diphenylanthracene.

Analysis of DPA Concentration in Films

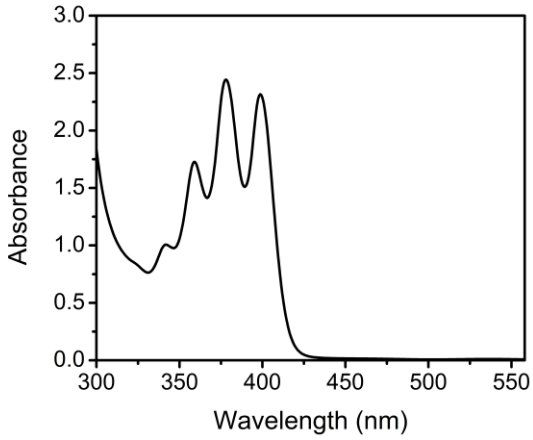

Figure S6. Absorbance spectra of thiol-ene film with 0.25 wt% DPA. The absorbance at 376 nm is used to calculate the DPA concentration.

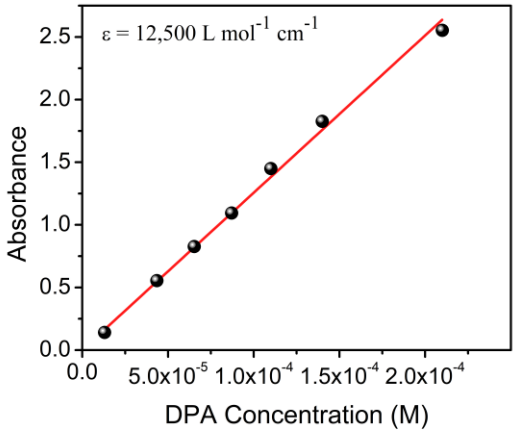

Figure S7. Absorbance values recorded for DPA $CHCl_3$ solutions at 376 nm. The extinction coefficient calculated using Beers-Lamberts law is shown.

$$c_{DPA} = \frac{A}{\varepsilon_{DPA} * l} = \frac{2.5}{12{,}500\ cm^{-1}\ M^{-1} \times 0.0265\ cm} = 0.0075\ M \qquad \text{(Eq. S1)}$$

$$wt\%\ DPA = \frac{c_{DPA} * MW_{DPA}}{D_{film}} \times 100 = \frac{0.0075\ M * 330.42\ g\ mol^{-1}}{1000\ g\ L^{-1}} \times 100 \qquad \text{(Eq. S2)}$$

$$= 0.249\ wt\%\ DPA$$

Leeching Experiments

To confirm the covalent attachment of **2**in the thiol-ene networks, films were submerged in $CHCl_3$ for 24 h and the supernatant was analyzed using UV-vis spectroscopy. Beer-Lambert law was used to calculate the % DPA from the film that leeched into the solution.

Table S1. Data used to calculate the % DPA that leeched out of the thiol-ene films.

Nominal DPA Conc. (wt%)	Wt. of Film (g)	Theoretical Wt. of DPA in film (mg)	Absorbance of Supernatant at 376 nm	Calculated DPA Conc. in solution (M)	Calculated Weight of DPA in solution (mg)	% DPA leeched in solution[a]
0.25	0.0735	0.18	0.003	2.40E-07	0.002	1.1
0.5	0.1232	0.62	0.025	2.99E-06	0.017	2.7
1.0	0.1442	1.4	0.021	1.68E-06	0.014	0.96
1.8	0.1108	1.9	0.034	2.72E-06	0.022	1.2
2.5	0.1394	3.5	0.062	4.96E-06	0.041	1.2
5.0	0.1196	6.0	0.186	1.49E-05	0.123	2.1

[a] The % DPA leeched into solution = Calculated weight of DPA in solution / theoretical weight of DPA in the film

Analysis of PdOEP Concentration in Films

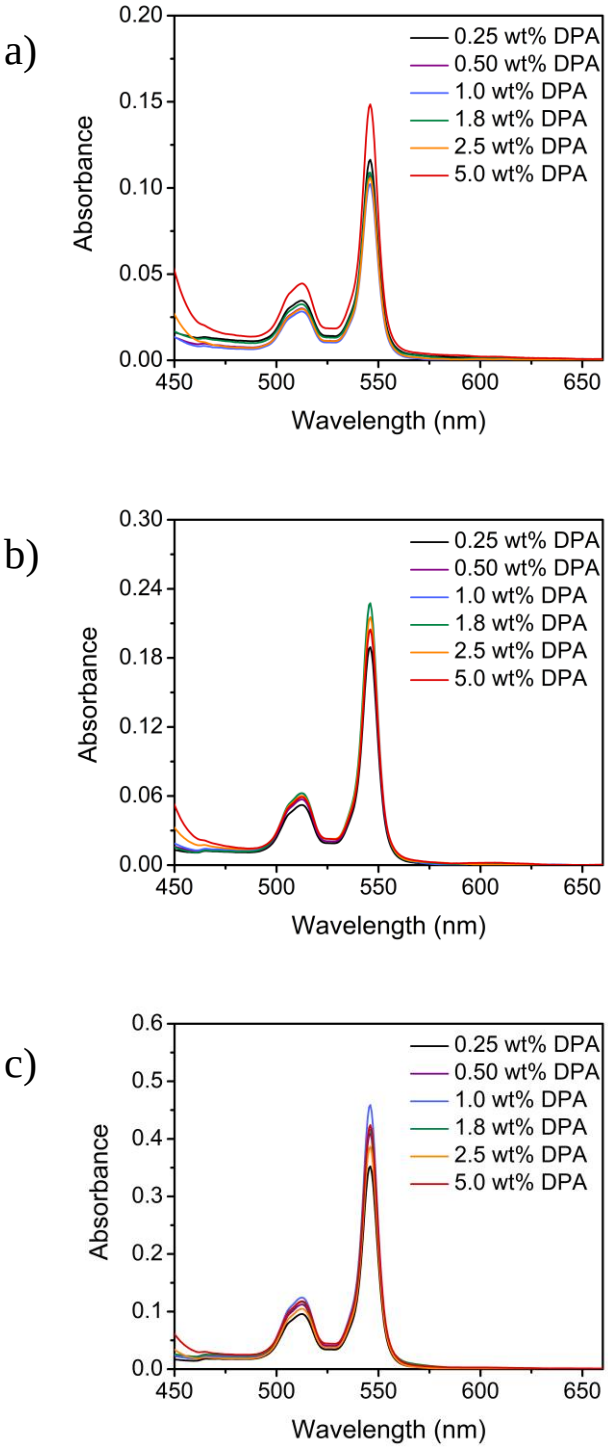

Figure S8. Absorbance spectra of thiol-ene films that were submerged in $CHCl_3$ solutions containing a) 0.038, b) 0.075, and c) 0.15 mg mL^{-1} PdOEP.

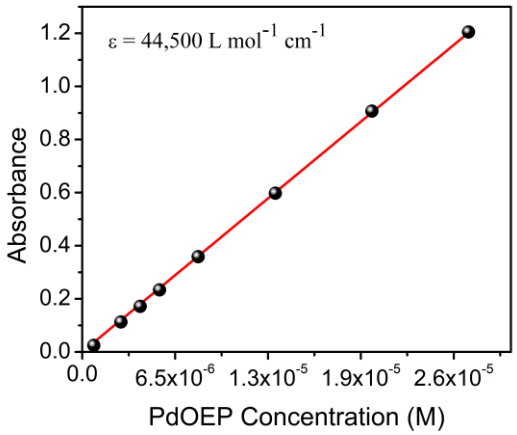

Figure S9. Absorbance values recorded for PdOEP $CHCl_3$ solutions at 546 nm. The extinction coefficient calculated using Beers-Lamberts law is shown.

$$c_{PdOEP} = \frac{A}{\varepsilon_{PdOEP} * l} = \frac{0.35}{44500\ cm^{-1}\ M^{-1} \times 0.0265\ cm} = 0.00030\ M \quad \text{(Eq. S3)}$$

$$wt\%\ PdOEP = \frac{c_{PdOEP} * MW_{PdOEP}}{D_{film}} \times 100 = \frac{0.00030\ M * 639.18\ g\ mol^{-1}}{1000\ g\ L^{-1}} \times 100 \quad \text{(Eq. S4)}$$

$$= 0.0190\ wt\%$$

Table S2. Data used to calculate the PdOEP concentrations in the thiol-ene films.

PdOEP Solution Concentration (mg mL^{-1})	DPA Concentration (wt%)	Absorbance at 546 nm	PdOEP Concentration in Film (M)	PdOEP Concentration in Film (wt%)
0.038	0.25	0.12	9.9E-05	0.005
	0.5	0.11	9.1E-05	0.005
	1.0	0.10	8.7E-05	0.005
	1.8	0.11	9.0E-05	0.005
	2.5	0.11	9.0E-05	0.005
	5.0	0.15	1.3E-04	0.007
0.075	0.25	0.19	1.6E-04	0.09
	0.5	0.21	1.7E-04	0.09
	1.0	0.23	1.9E-04	0.01
	1.8	0.23	1.9E-04	0.01
	2.5	0.22	1.8E-04	0.01
	5.0	0.21	1.7E-04	0.01
0.15	0.25	0.35	3.0E-04	0.02
	0.5	0.41	3.5E-04	0.02
	1.0	0.46	3.9E-04	0.02
	1.8	0.42	3.5E-04	0.02
	2.5	0.39	3.3E-04	0.02
	5.0	0.42	3.6E-04	0.02

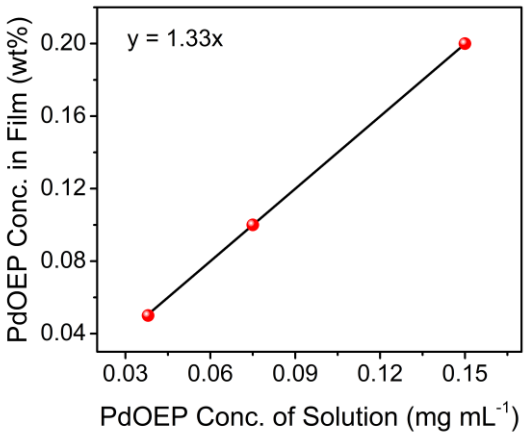

Figure S10. Calculated wt% PdOEP infused into thiol-ene films as a function of the PdOEP concentration in the $CHCl_3$ solution the films were submerged in.

Direct Fluorescence of PdOEP doped Films

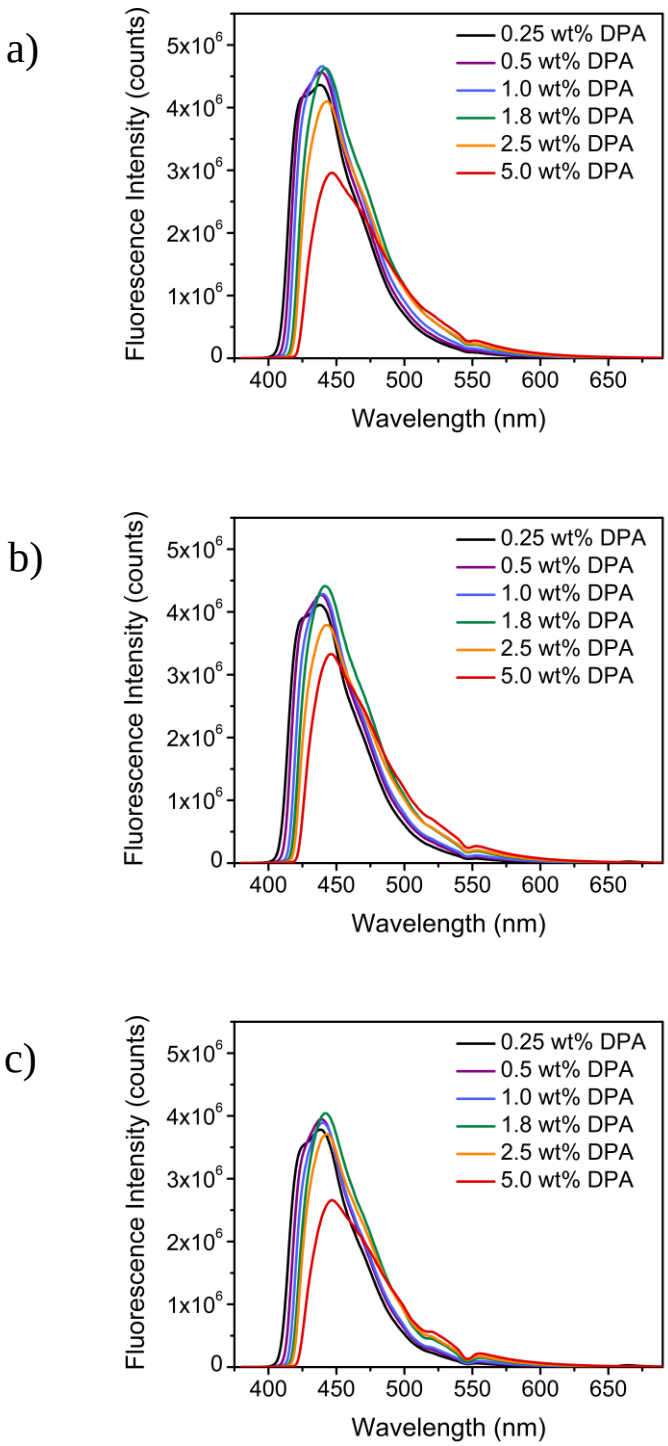

Figure S11. Direct fluorescence emission spectra of thiol-ene networks doped with a) 0.005, b) 0.01, and c) 0.02 wt% PdOEP (λ_{ex} = 375 nm).

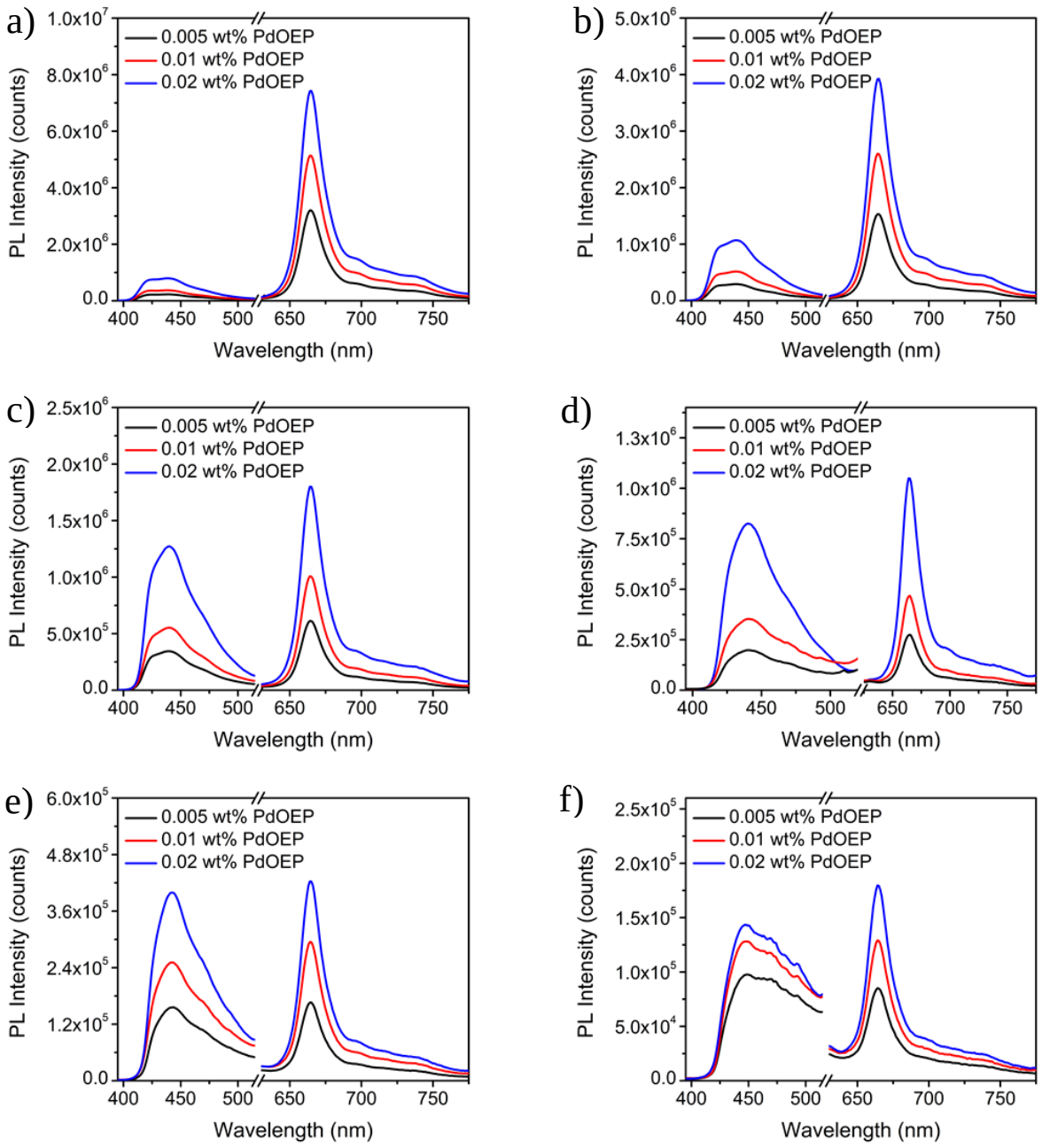

Figure S12. Photoluminescence emission from PdOEP doped thiol-ene films comprised of a) 0.25, b) 0.5, c) 1.0, d) 1.8, e) 2.5, and f) 5.0 wt% DPA (λ_{ex} = 544 nm). A break from 520 to 630 nm is included to exclude the excitation peak for clarity.

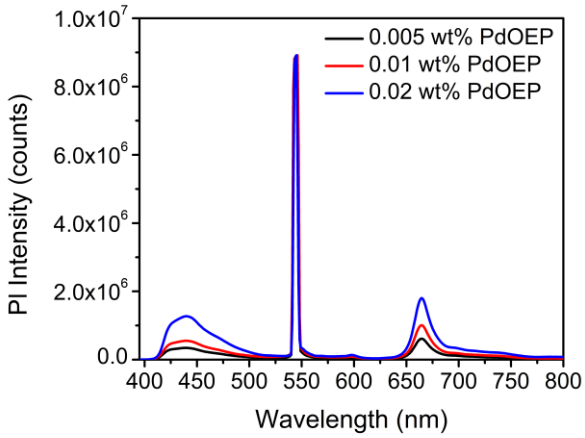

Figure S13. Photoluminescence emission from PdOEP doped thiol-ene films comprised of 1.0 wt% DPA (λ_{ex} = 544 nm).

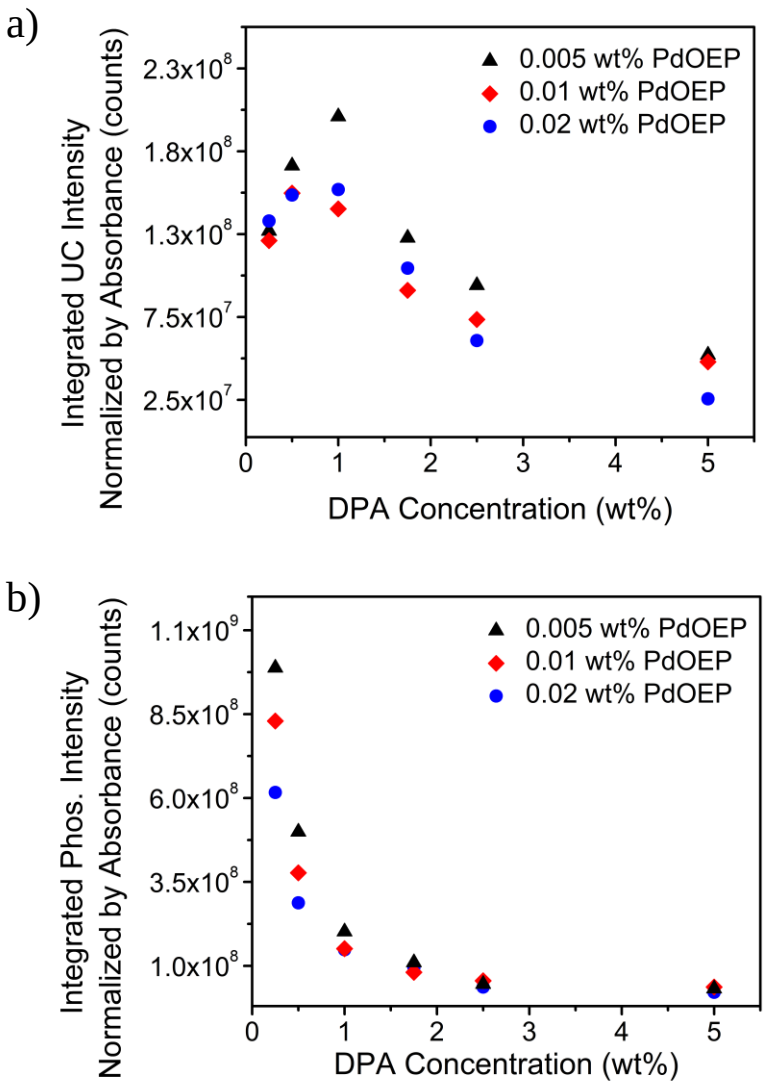

Figure S14. Integrated upconverted emission (a) and phosphorescence (b) intensities normalized by the absorbance from thiol-ene films with various PdOEP concentrations as a function of DPA concentration.