Supplementary information

4-Bis (4-aminophenoxy)phenoxy derivitized phthalocyanine conjugated to metallic nanoparticles, searching for enhanced optical limiting materials.

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5-level model rate equations S1-S7 follow

$$\frac{dN_o}{dt} = -\frac{\delta_0 I N_0}{\hbar\omega} - \frac{\beta I^2}{2\hbar\omega} + \frac{N_0}{\tau_0} + \frac{N_2}{\tau_1} \qquad \text{(S1)}$$

$$\frac{dN_1}{dt} = \frac{\delta_1 I N_1}{\hbar\omega} + \frac{\delta_0 I N_0}{\hbar\omega} - \frac{N_0}{\tau_0} - \frac{N_0}{\tau_{isc}} + \frac{N_1}{\tau_1} \qquad \text{(S2)}$$

$$\frac{dN_2}{dt} = \frac{\delta_1 I N_1}{\hbar\omega} + \frac{\beta I^2}{2\hbar\omega} - \frac{N_1}{\tau_1} \qquad \text{(S3)}$$

$$\frac{dN_3}{dt} = -\frac{\delta_2 I N_3}{\hbar\omega} - \frac{N_2}{\tau_2} + \frac{N_0}{\tau_{isc}} + \frac{N_3}{\tau_3} \qquad \text{(S4)}$$

where δ_0, δ_1 and δ_2 are the ground, singlet and triplet excited state absorption cross section respectively, $\hbar$ is Planck's constant, ω is the frequency of light, the N_i values represent the populations in the different states; β is the two photon absorption (TPA) cross-section, the τ_i values are the lifetimes of the excited states; and τ_{isc} is the lifetime of intersystem crossing. The intensity transmitted through the sample is represented as I.

The intensity transmitted through the sample (I) is given by equations

$$\frac{dI}{dt} = \frac{c\ dI}{n_r dz} = \frac{cI}{n_r}[\delta_0 N_1 + \delta_1 N_2 + \delta_2 N_3] \qquad \text{(S5)}$$

With $$I = I_{00}\left(\frac{\omega_0^2}{\omega^2(z)}\right)exp\left(-\frac{t^2}{\tau_p^2}\right)exp\left(-\frac{2r^2}{\omega^2(z)}\right) \quad \text{(S6)}$$

$$\omega(z) = \omega_0\sqrt{\left\{1+\left(\frac{z}{z_0}\right)^2\right\}};\quad z_0 = \frac{\pi\omega_0^2}{\lambda} \quad \text{(7)}$$

where n_r is the refractive index (n_r = 1.479 in DMSO), c is the speed of light in vacuum, I_{00} is the peak intensity at the focus of Guassian beam; τ_p is the input pulse width; $\boldsymbol{\omega}_0$ is beam waist at focus, z_0 is Rayleigh range and r is the radius of the aperture. dI/dz in eq.S5 describes the change of photon flux with propagation of laser light through the sample with z as the position of the sample in the beam profile.

Supporting Figures

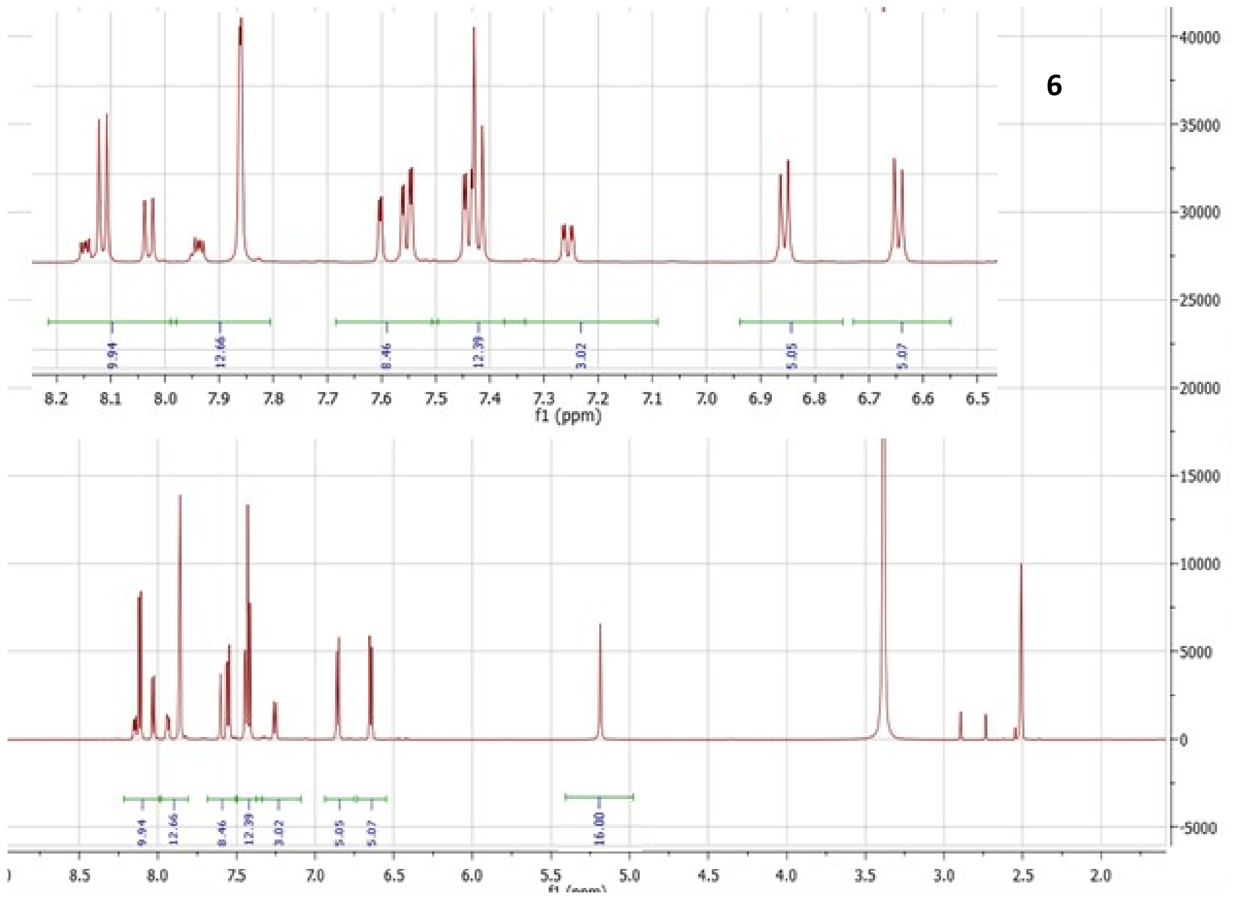


Fig. S1 NMR spectrum of complex **6** in DMSO-d_6 (insert, expanded section of the spectra)

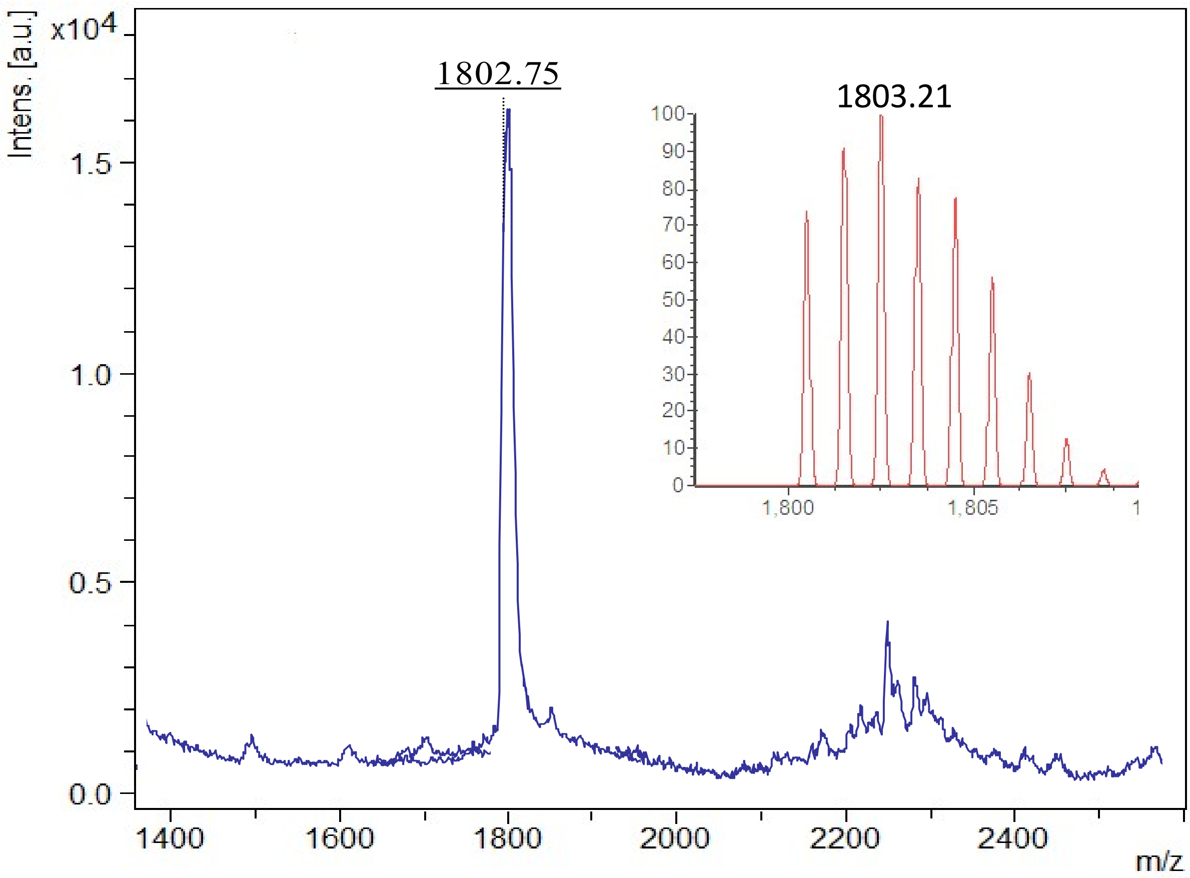


Fig. S2: MALDI-TOF mass spectra of complex **6** (insert, simulated isotropic mass distribution)

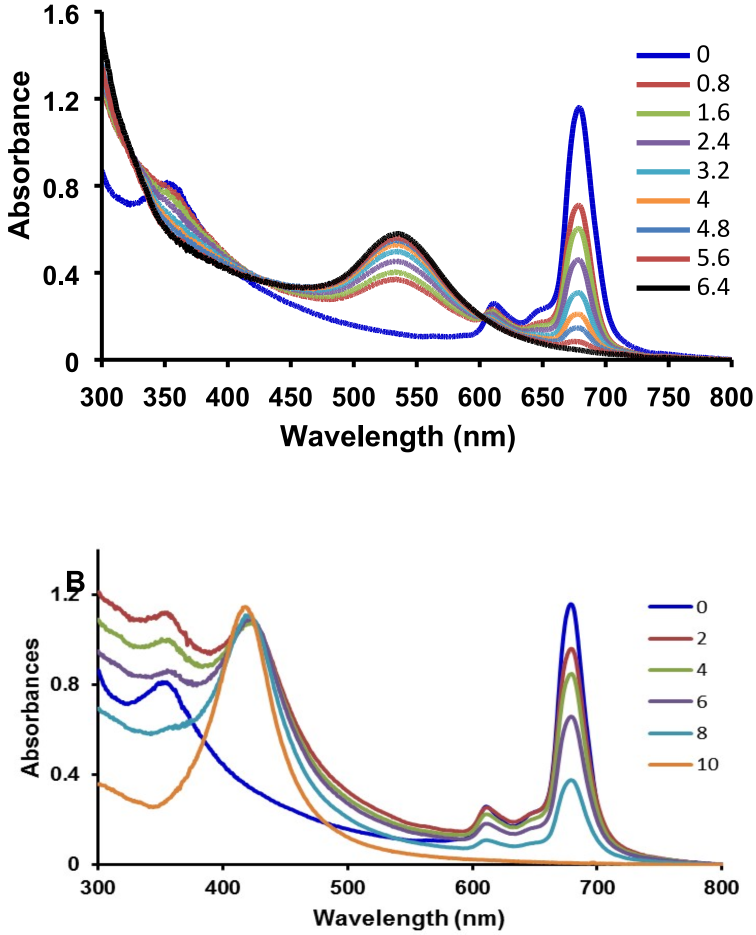
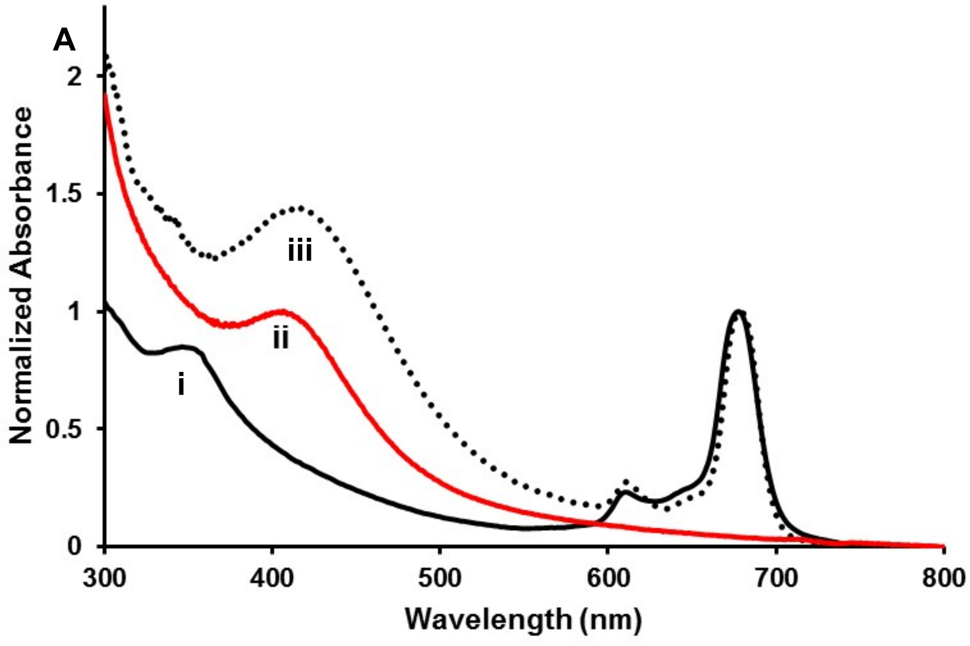


Fig. **S3**: Absorption spectra of 3 (5.0 µM) in aqeous solution containing different ratio of AuNPs or AgNPs



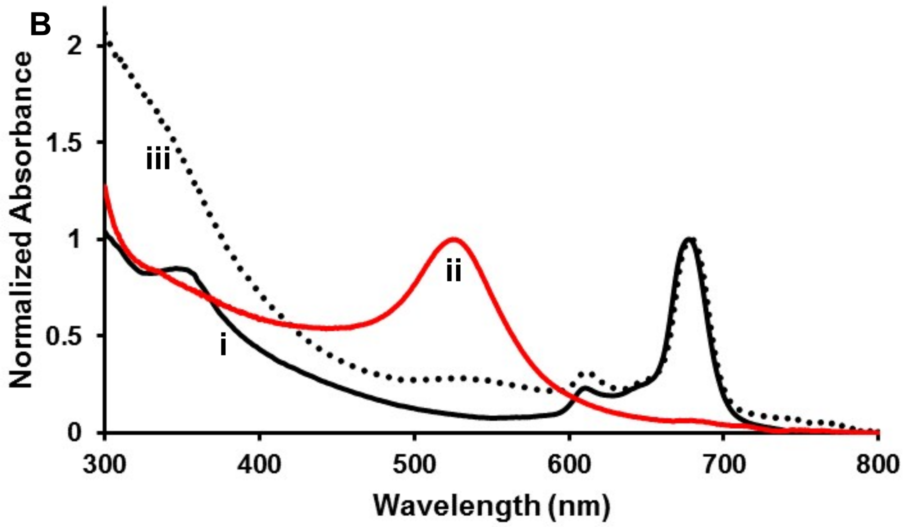


Fig. S4: Absorption spectra of (A) **6** (i), OA-AgNPs (ii) and **6**SA-AgNPs (iii), (B), **6** (i) GSH-AuNPs (ii) and **6**CB-AuNPs (iii) in DMSO.

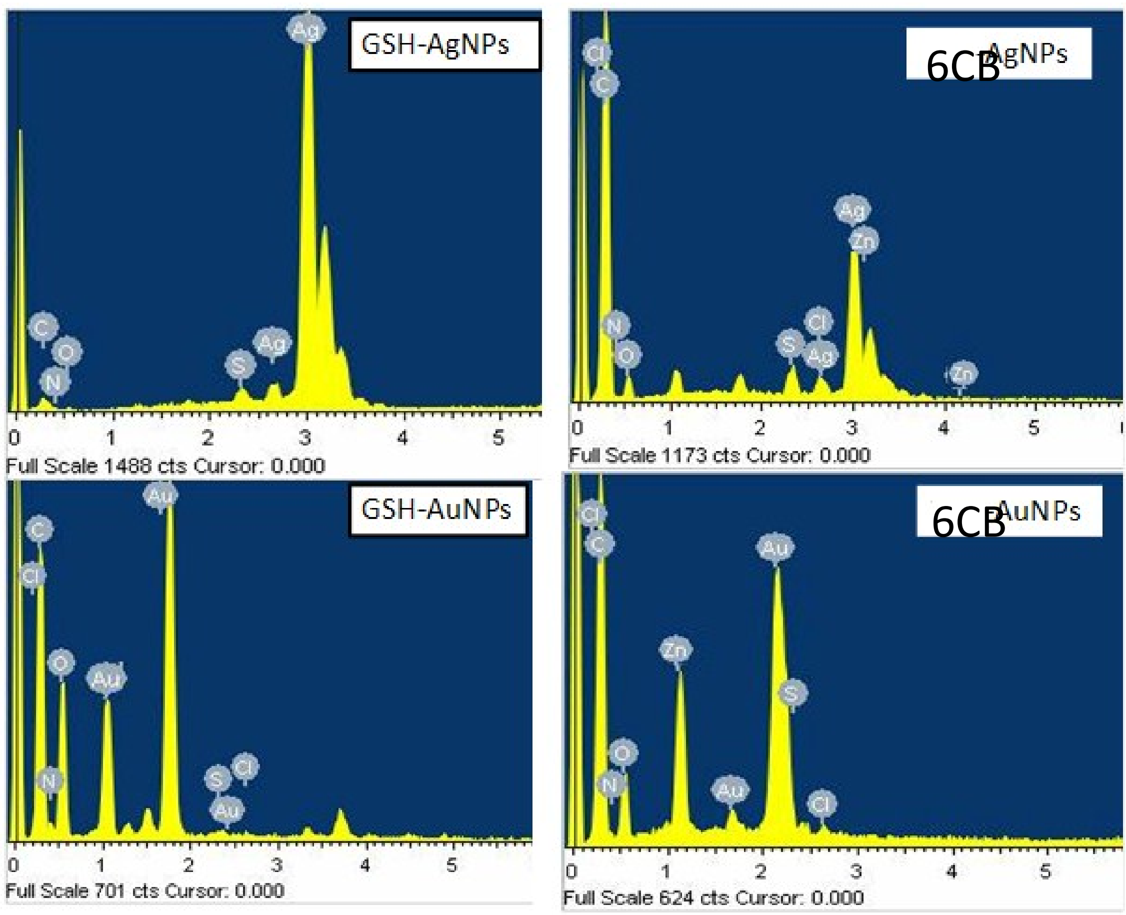


Fig. S5: Representative EDX spectra of glutathione functionalized nanoparticles alone and when conjugated to complex **6**

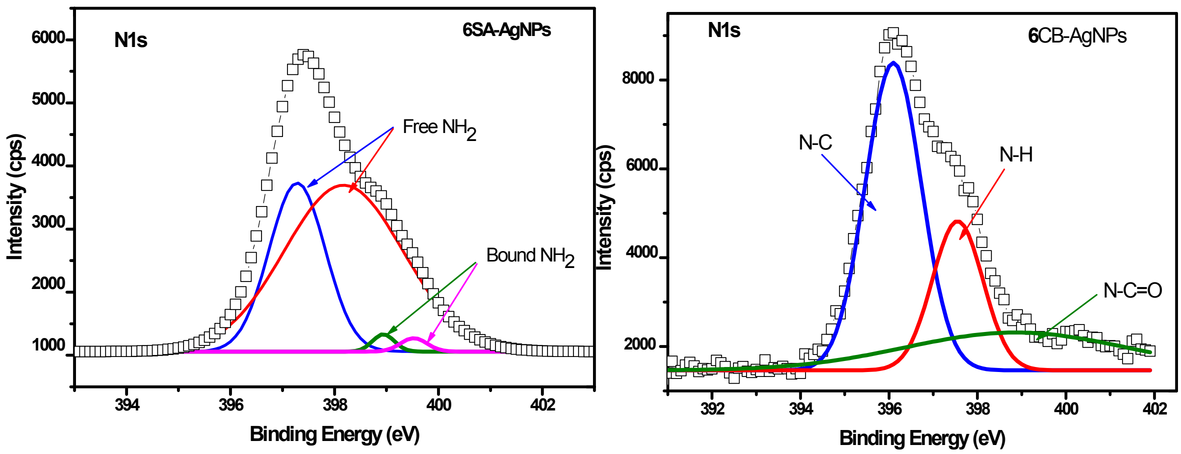


Fig. S6: High resolution XPS spectrum of N 1s for **6**SA-AgNPs and **6**CB-AgNPs

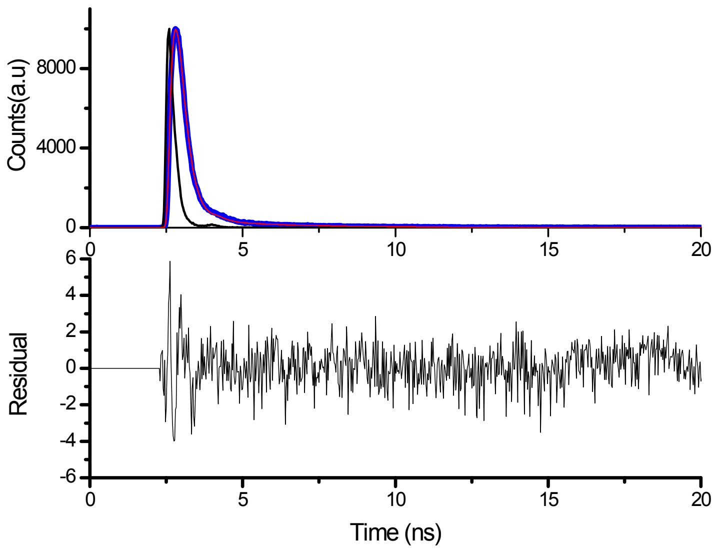


Fig S7: Fluorescence lifetime decay curve of complex **6** in DMSO

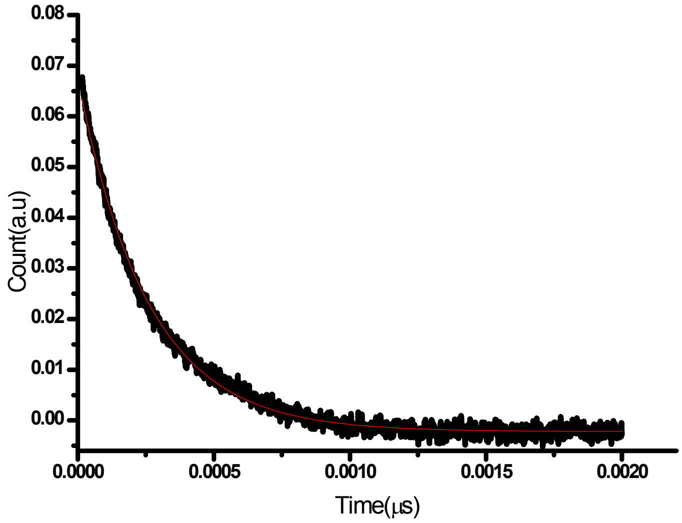


Fig. S8: Triplet decay curve of **6**CB-AuNPs in DMSO

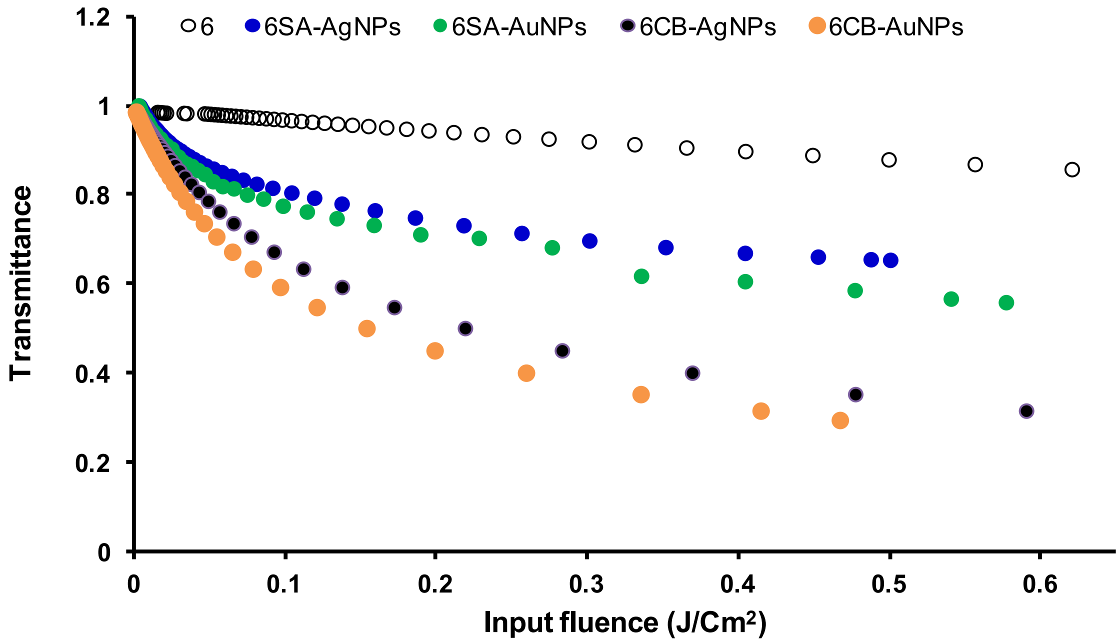


Fig. S9: Transmission *vs.* input fluence (I_o) curve for complex **6** and its nanoconjugates

Table S1. TD-DFT spectra of the B3LYP optimized geometries for **6** with a four-fold symmetric set of attachments calculated with the CAM-B3LYP functional and 6-31G(d) basis sets.

		6					
Band[a]	**#**[b]	**Calc**[c]			**Exp**[d]		**Wave Function**[e] =
Q	**1**	16.0	626	(0.49)	14.7	680	**93% $1a_{1u}$ → $1e_g$*;** …
	2	16.1	620	(0.72)			**93% $1a_{1u}$ → $1e_g$*;** …
B1	**12**	32.4	309	(0.70)	28.7	348	**41% $1a_{2u}$ → $1e_g$*;** 11% H−3^{Ph} → $1e_g$*; …
	13	32.6	307	(1.13)			**45% $1a_{2u}$ → $1e_g$*;** 16% H−4^{Ph} → $1e_g$*; 11% $1b_{2u}$ → $1e_g$*; …
B2	**18**	34.4	291	(0.38)	---	---	42% $2a_{2u}$ → $1e_g$*; …
	19	34.4	290	(0.43)	---	---	44% $2a_{2u}$ → $1e_g$*; …

a − Band assignment described in the text. b − The number of the state assigned in terms of ascending energy within the TD-DFT calculation. c − Calculated band energies ($10^3.cm^{-1}$), wavelengths (nm) and oscillator strengths in parentheses (f). d − Observed energies ($10^3.cm^{-1}$) and wavelengths (nm) in Figure 1. e − The wave functions based on the eigenvectors predicted by TD-DFT with one-electron transitions associated with Gouterman's 4-orbital model highlighted in bold. The symmetry notations in each case used refer to the D_{4h} symmetry of the parent monomeric Pc(−2) ligand to facilitate a comparison. Only one-electron transitions that provide a greater than 10% contribution are included and a Ph superscript is used to denote MOs that are localized primarily on the phenoxy substituents.