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

\[
\frac{dN_0}{dt} = -\frac{\delta_0 I N_0}{\hbar \omega} - \frac{\beta I^2}{2\hbar \omega} + \frac{N_0}{\tau_0} + \frac{N_2}{\tau_1} \]  
(S1)

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

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

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

where \(\delta_0, \delta_1\) and \(\delta_2\) are the ground, singlet and triplet excited state absorption cross section respectively, \(\hbar\) is Planck’s constant, \(\omega\) is the frequency of light, the \(N_i\) values represent the populations in the different states; \(\beta\) is the two photon absorption (TPA) cross-section, the \(\tau_i\) values are the lifetimes of the excited states; and \(\tau_{isc}\) 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

\[
\frac{dl}{dt} = c \frac{dl}{n_r dz} = c \frac{l}{n_r} \left[ \delta_0 N_1 + \delta_1 N_2 + \delta_2 N_3 \right] \] 
(S5)
\[ I = I_{00} \left( \frac{\omega_0^2}{\omega^2(z)} \right) \exp\left( -\frac{t^2}{\tau_p^2} \right) \exp\left( -\frac{2r^2}{\omega^2(z)} \right) \]  
With \( \omega(z) = \omega_0 \sqrt{1 + \left( \frac{Z}{Z_0} \right)^2}; \ Z_0 = \frac{\pi \omega_0^2}{\lambda} \)  

(56)

(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; \( \tau_p \) is the input pulse width; \( \omega_0 \) 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 aqueous solution containing different ratio of AuNPs or AgNPs
**Fig. S4:** Absorption spectra of (A) 6 (i), OA-AgNPs (ii) and 6SA-AgNPs (iii), (B), 6 (i) GSH-AuNPs (ii) and 6CB-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 6SA-AgNPs and 6CB-AgNPs

Fig S7: Fluorescence lifetime decay curve of complex 6 in DMSO
**Fig. S8:** Triplet decay curve of 6CB-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.

<table>
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<th>Band#</th>
<th>Calc</th>
<th>Exp</th>
<th>Wave Function</th>
</tr>
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<tbody>
<tr>
<td>Q</td>
<td>1</td>
<td>16.0 626 (0.49)</td>
<td>14.7 680</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>16.1 620 (0.72)</td>
<td>93% 1a_1u → 1e_g*; ...</td>
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<tr>
<td>B1</td>
<td>12</td>
<td>32.4 309 (0.70)</td>
<td>38.7 348</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>32.6 307 (1.13)</td>
<td>45% 1a_2u → 1e_g*; 16% H−4^h → 1e_g*; 11% 1b_2u → 1e_g*; ...</td>
</tr>
<tr>
<td>B2</td>
<td>18</td>
<td>34.4 291 (0.38)</td>
<td>--- ---</td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>34.4 290 (0.43)</td>
<td>--- ---</td>
</tr>
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</table>

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 (10^13 cm^-1), wavelengths (nm) and oscillator strengths in parentheses (f). d – Observed energies (10^13 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.