Supporting Information

Exciting clusters, what does off-resonance actually mean?

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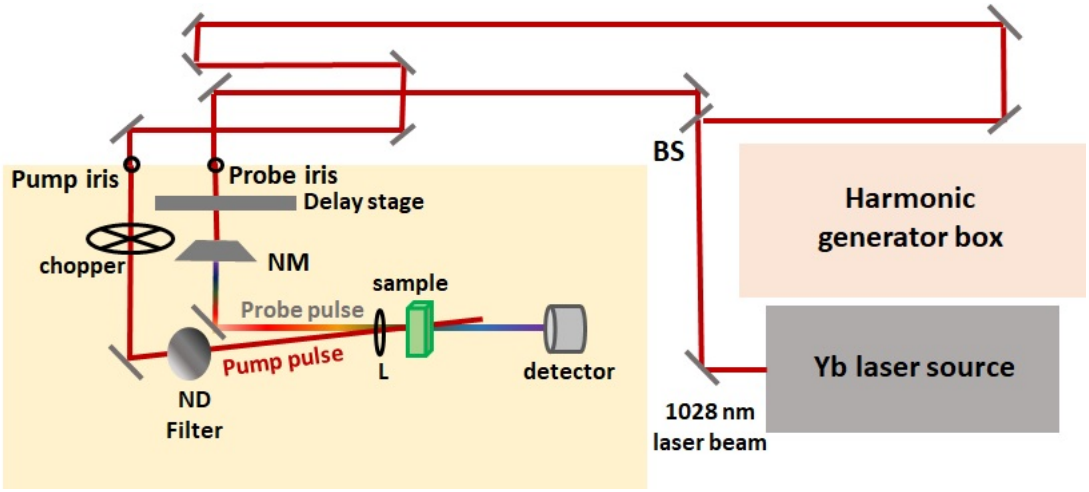

Scheme S1. Fs Transient absorption spectrometer set up: amplified pulses from Yb laser are split into two parts using a beam splitter (BS). One part is used to pump a tunable pump pulse. The other part is delayed in a delay stage, and then focused into a nonlinear medium (NM), where white light is generated. The generated probe light is overlapped with pump light in the sample. The chopper is periodically closing and opening the pump beam in order to take the probe intensity measurements of the excited and non-excited sample. The pump pulse power can be controlled using a neutral density filter (ND Filter). In order to record excited state absorbance spectrum at different powers, a power meter was used right after the ND filter and just before the laser beam gets focused on the sample.

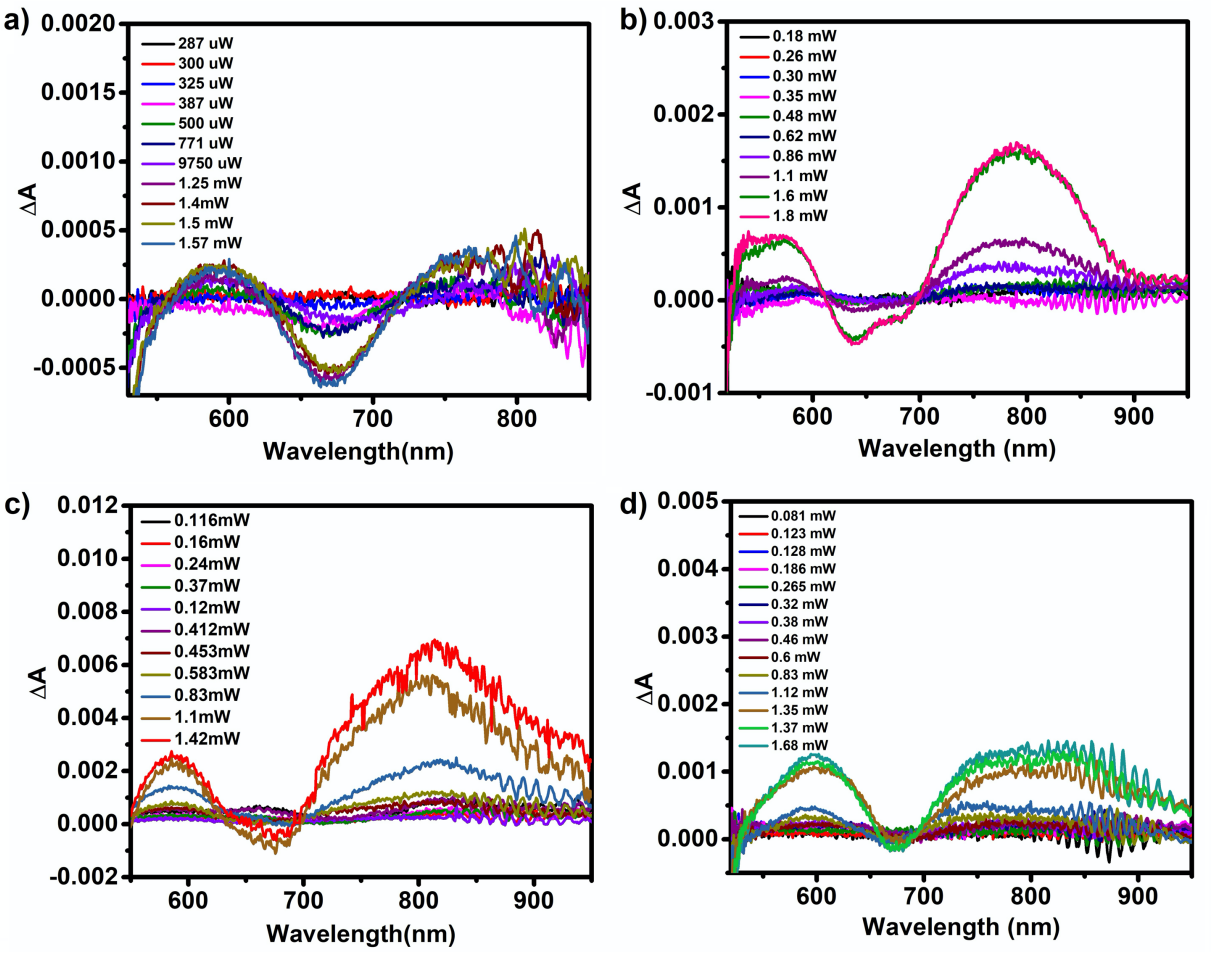

Figure S2. Two-photon induced excited state absorption spectra of a) $Au_{25}(GS)_{18}$, b) $Au_{25}(Capt)_{18}$, c) $Au_{25}(Me_2PhS)_{18}$, and d) $Au_{25}(PET)_{18}$ excited with 1028 nm pulsed laser light to illustrate that the generation and the growth of the two-photon induced excited state absorption is power dependent and when clusters reach their threshold start to show the two-photon respond. All samples have matched absorbances at 514nm.

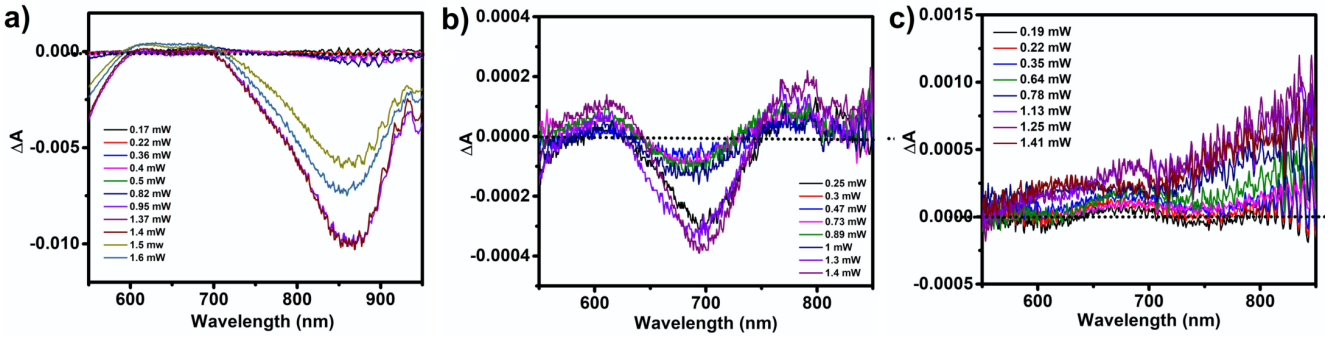

Figure S3. *Top panel:* Two-photon induced excited state absorption spectra of a) $Au_{18}(GS)_{14}$, b) $Au_{18}(Capt)_{14}$, and c) $Au_{18}(CyHT)_{14}$ excited with 1028 nm pulsed laser light to illustrate that the generation and the growth of the two-photon induced excited state absorption is power dependent and when clusters reach their threshold start to show the two-photon respond. All samples have matched absorbances at 514nm.

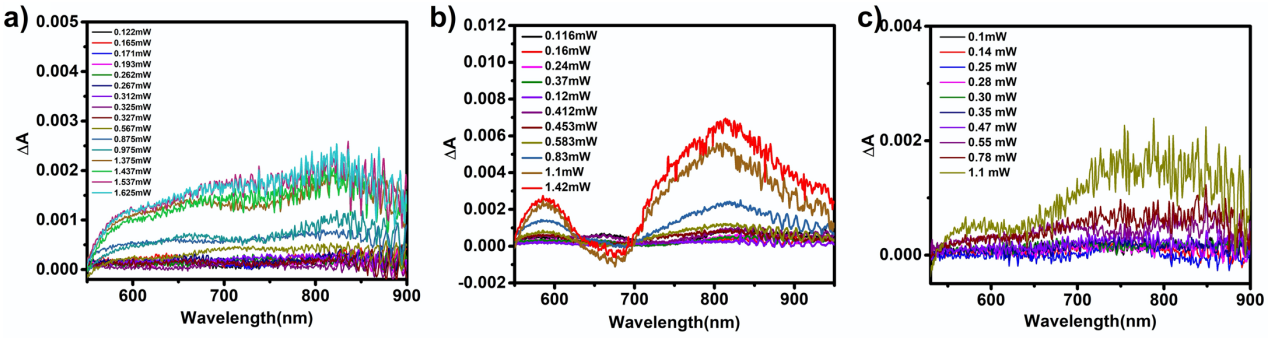

Figure S4. Two-photon induced excited state absorption spectra of a) $Ag_{25}(Me_2SPh)_{18}$, b) $Au_{25}(Me_2SPh)_{18}$, and c) the resulting alloy cluster synthesized using these two clusters. excited with 1028 nm pulsed laser light to illustrate that the generation and the growth of the two-photon induced excited state absorption is power dependent and when clusters reach their threshold start to show the two-photon respond. All samples have matched absorbances at 514nm.

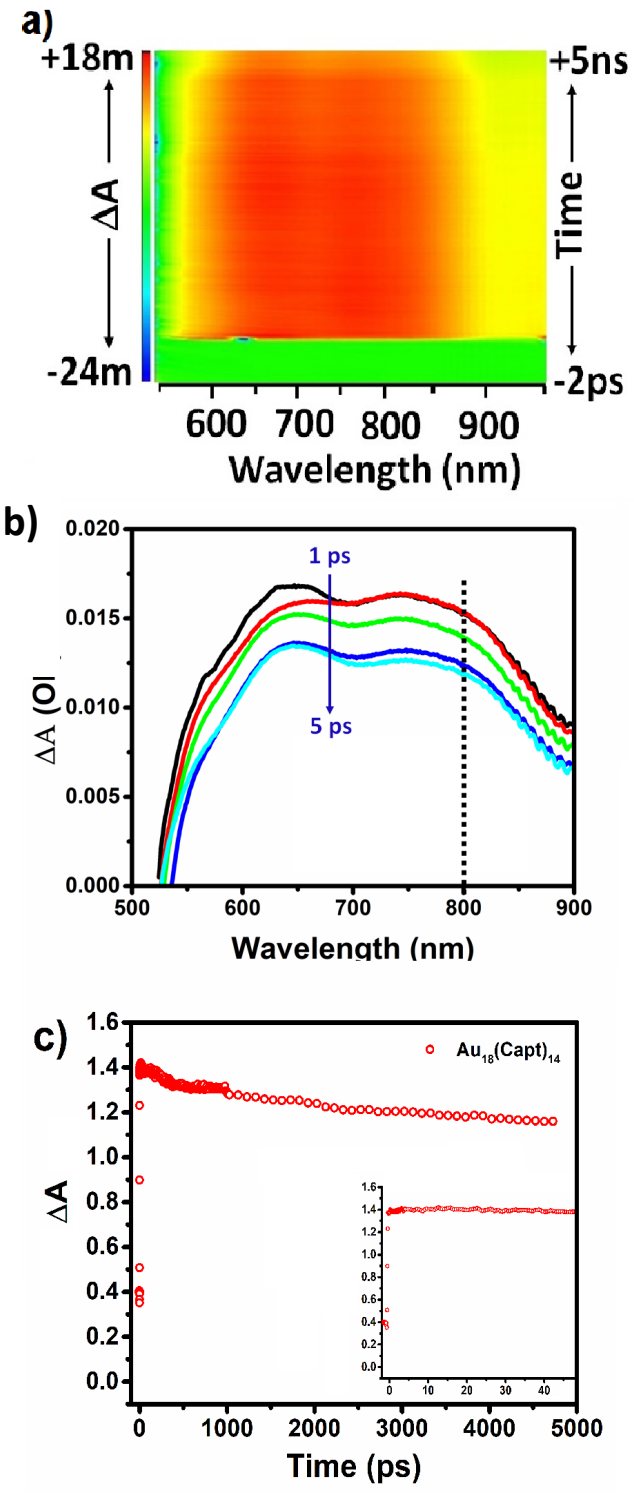

Figure S5. a) 3D transient absorption surface for $Au_{18}(Capt)_{14}$ obtained with 514 nm laser excitation, b) Transient absorption spectra between 1 ps - 5 ns d c) kinetic trace for the induced absorbance at 800 nm (inset shows the same data over a shorter timescale to illustrate the short lifetime component).

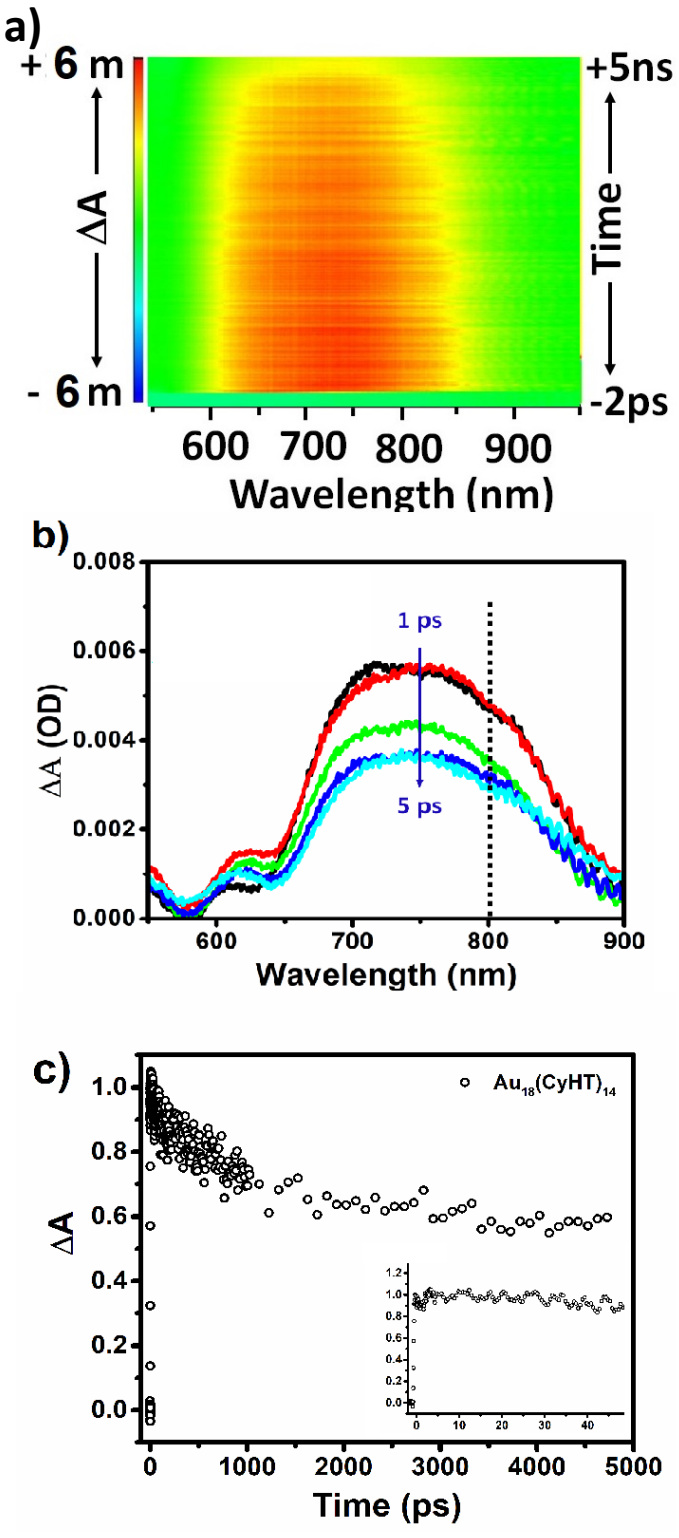

Figure S6. a) 3D transient absorption surface for $Au_{18}(CyHT)_{14}$ obtained with 514 nm laser excitation, b) Transient absorption spectra between 1 ps - 5 ns d c) kinetic trace for the induced absorbance at 800 nm (inset shows the same data over a shorter timescale to illustrate the short lifetime component).

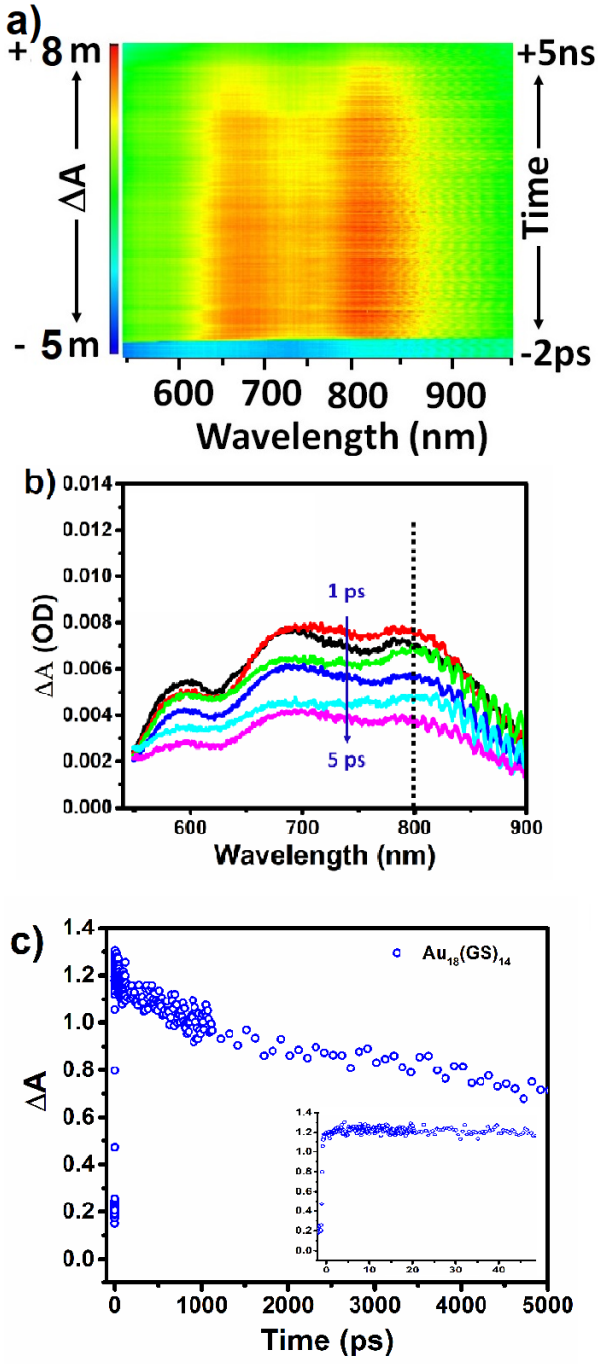

Figure S7. a) 3D transient absorption surface for $Au_{18}(GS)_{14}$ obtained with 514 nm laser excitation, b) Transient absorption spectra between 1 ps - 5 ns d c) kinetic trace for the induced absorbance at 800 nm (inset shows the same data over a shorter timescale to illustrate the short lifetime component).

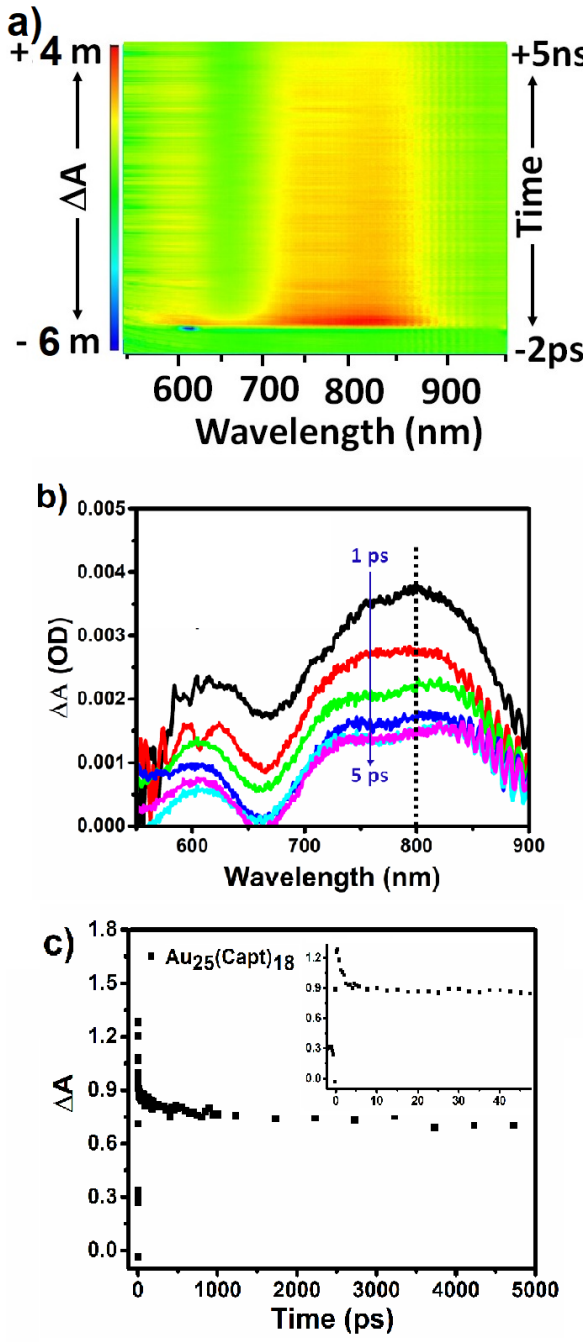

Figure S8. a) 3D transient absorption surface for $Au_{25}(Capt)_{18}$ obtained with 514 nm laser excitation, b) Transient absorption spectra between 1 ps - 5 ns d c) kinetic trace for the induced absorbance at 800 nm (inset shows the same data over a shorter timescale to illustrate the short lifetime component).

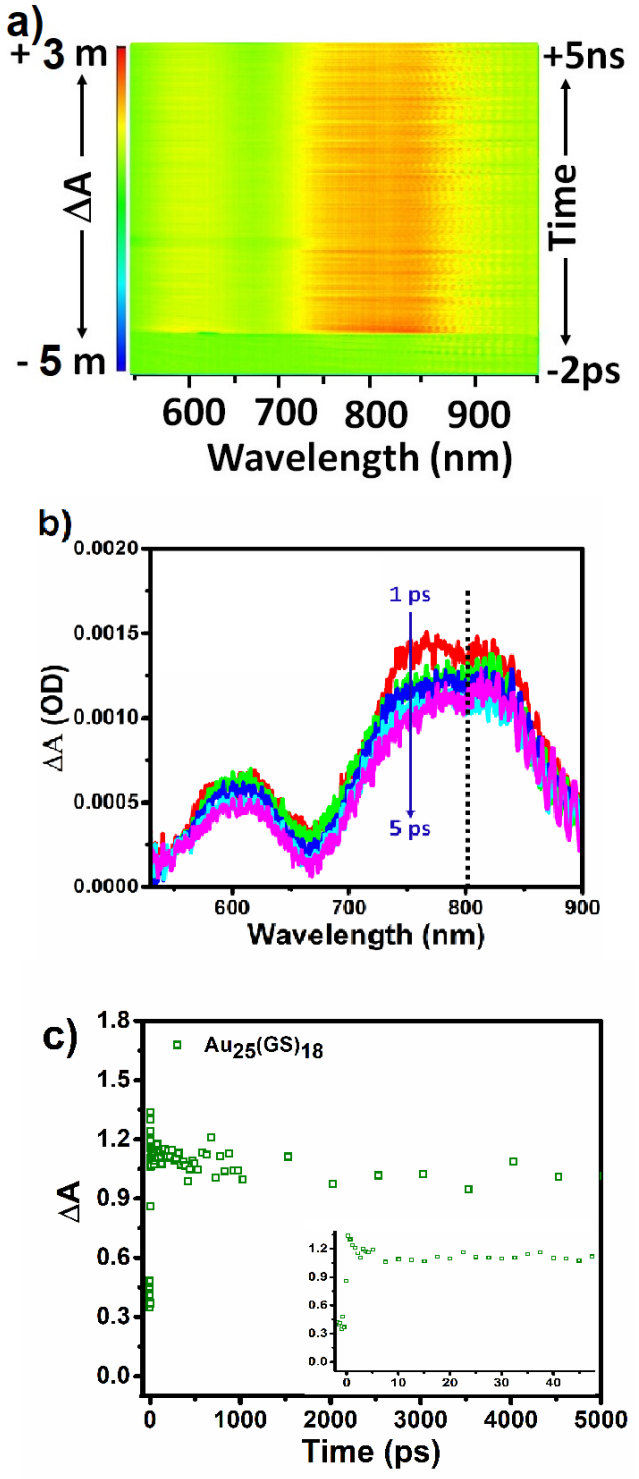

Figure S9. a) 3D transient absorption surface for $Au_{25}(GS)_{18}$ obtained with 514 nm laser excitation, b) Transient absorption spectra between 1 ps - 5 ns d c) kinetic trace for the induced absorbance at 800 nm (inset shows the same data over a shorter timescale to illustrate the short lifetime component).

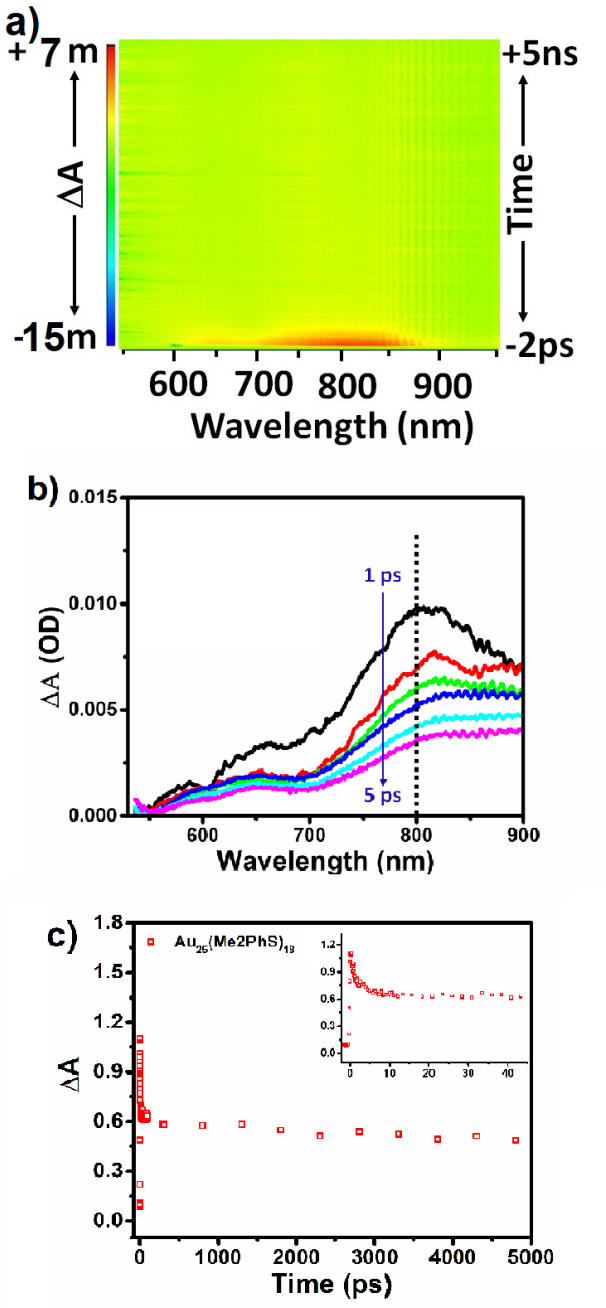

Figure S10. a) 3D transient absorption surface for $Au_{25}(Me_2PhS)_{18}$ obtained with 514 nm laser excitation, b) Transient absorption spectra between 1 ps - 5 ns d c) kinetic trace for the induced absorbance at 800 nm (inset shows the same data over a shorter timescale to illustrate the short lifetime component).

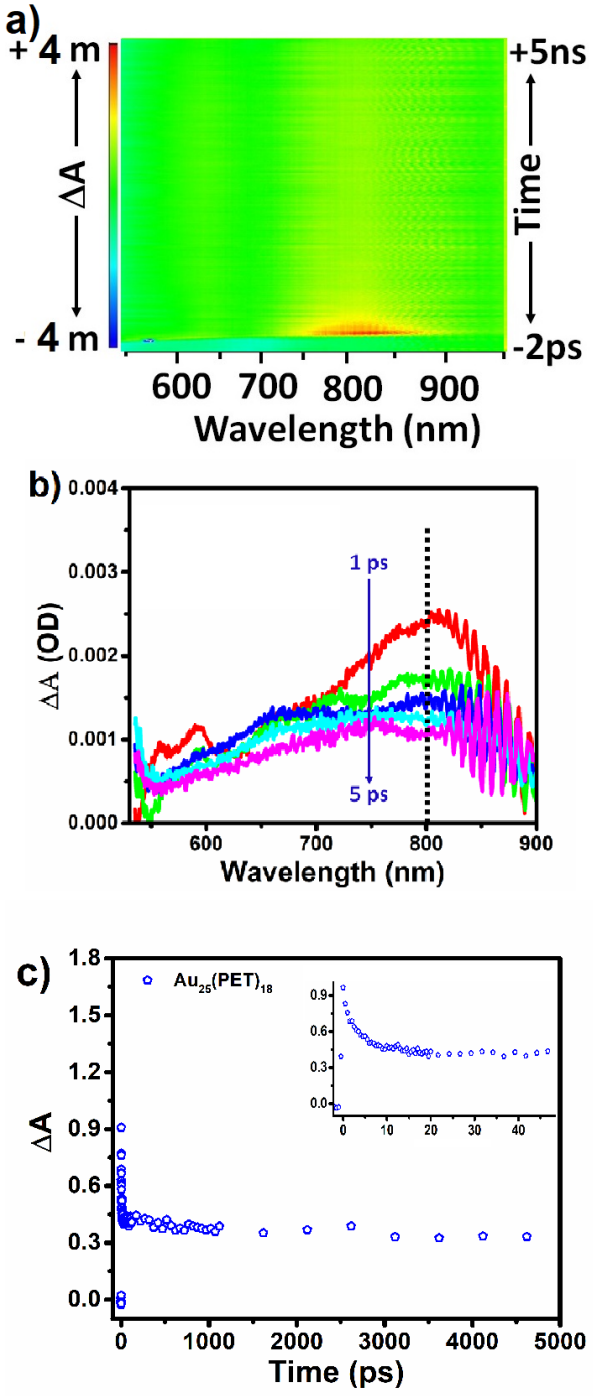

Figure S11. a) 3D transient absorption surface for $Au_{25}(PET)_{18}$ obtained with 514 nm laser excitation, b) Transient absorption spectra between 1 ps - 5 ns d c) kinetic trace for the induced absorbance at 800 nm (inset shows the same data over a shorter timescale to illustrate the short lifetime component).

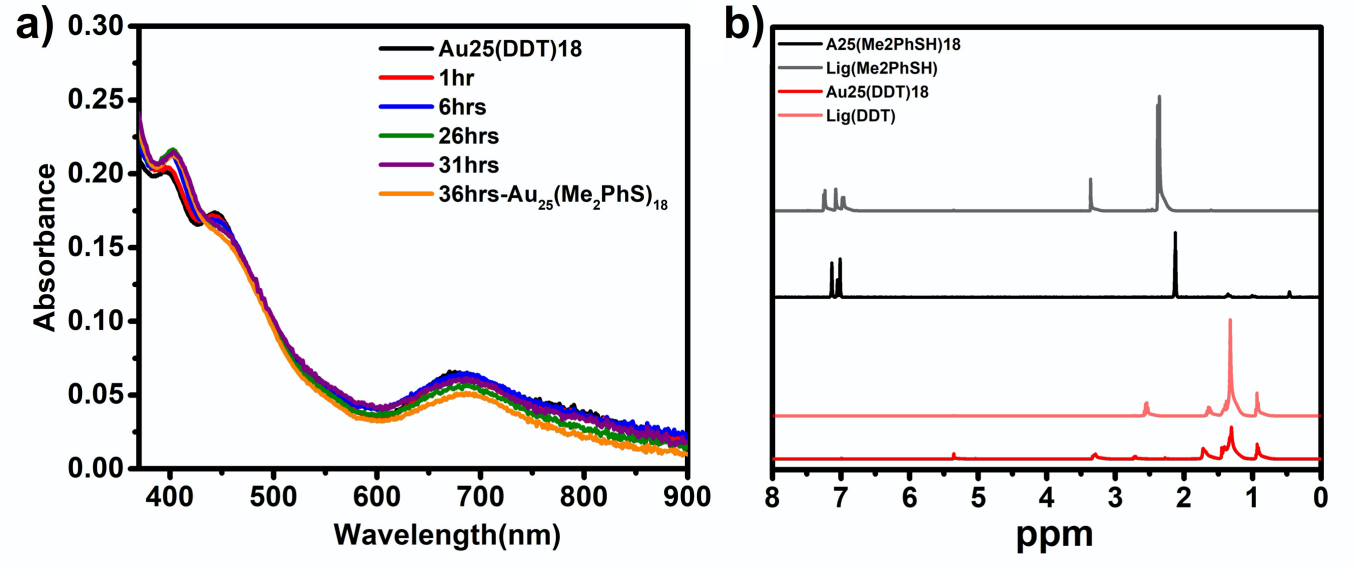

Figure S12. Kinetics of the ligand exchange reaction on $Au_{25}(DDT)_{18}$ to yield $Au_{25}(Me_2Ph_S)_{18}$ in 36 hrs, and b) ^{1}H-NMR on $Au_{25}(DDT)_{18}$ and $Au_{25}(Me_2Ph_S)_{18}$ to show the completion of the ligand exchange reaction.

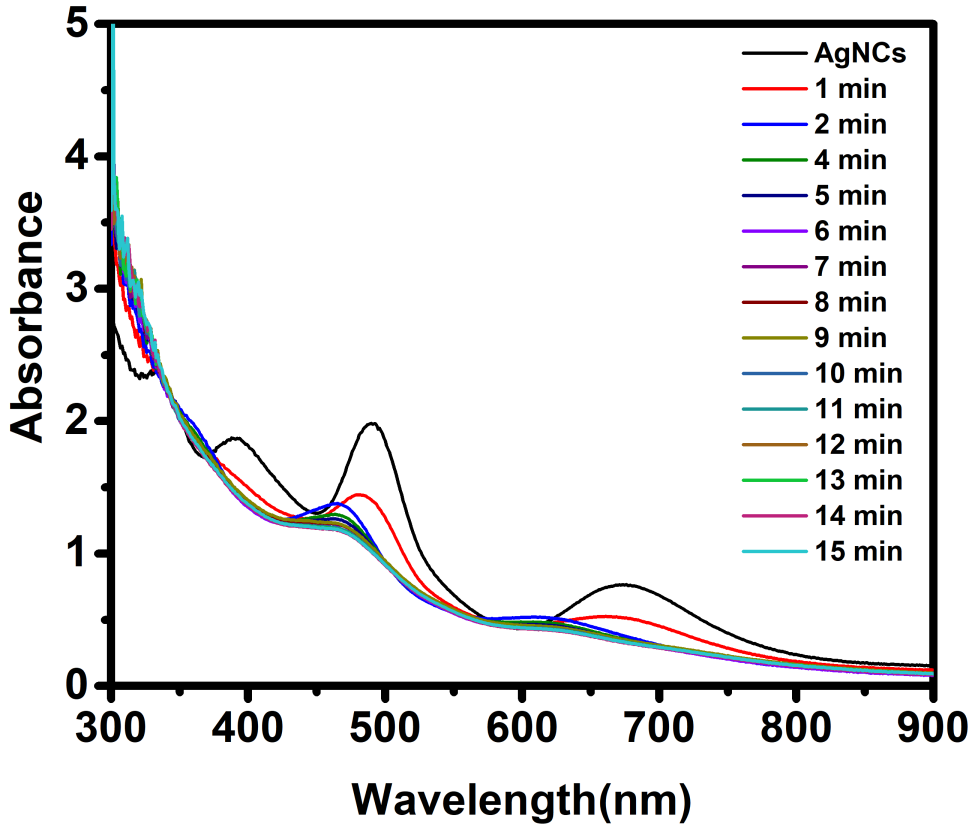

Figure S13. Kinetics of the alloying reaction between $Ag_{25}(Me_2Ph_S)_{18}$ and $Au_{25}(Me_2Ph_S)_{18}$ in 15 minutes. The black trace is the starting cluster which is $Ag_{25}(Me_2Ph_S)_{18}$ and the cyan blue trace is the $Au_{25}(Me_2Ph_S)_{18}$. This reaction is completed after 15 minutes.

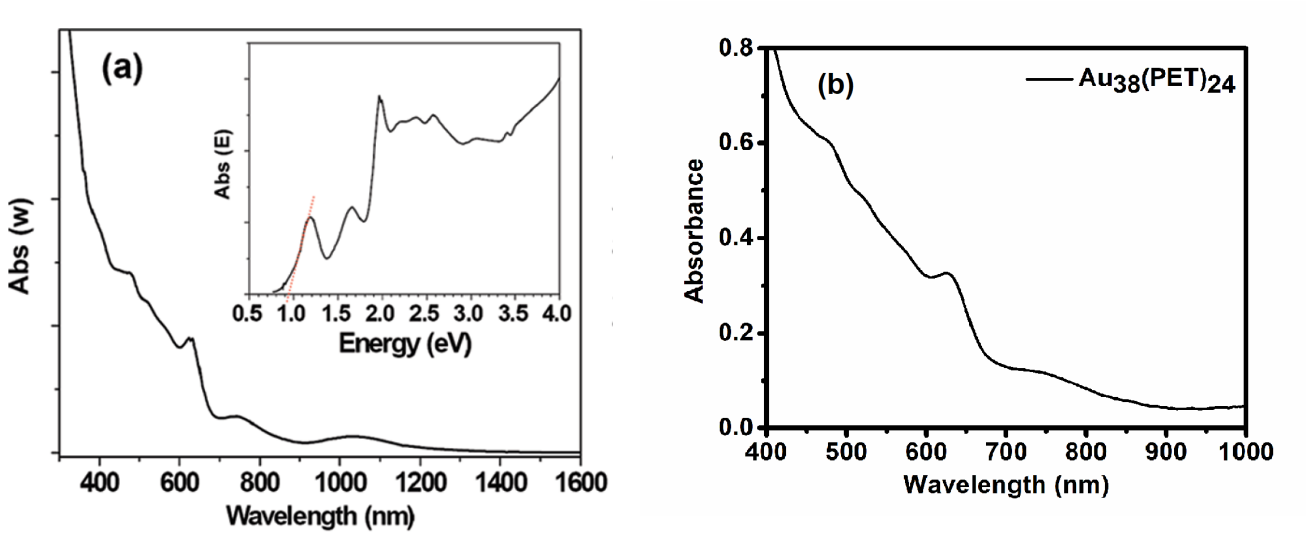

Figure S14. Steady-state absorbance spectrum of $Au_{38}(PET)_{24}$ a) adapted from reference 49 to exhibit electronic transitions in the NIR (centred at ~ 1050nm and b) experimentally acquired with a Varian Cary 60 UV-Vis spectrophotometer which shows characteristic series of absorbance features up to 1000 nm and due to detector limitations of the spectrometer we are not able to observe the electronic transition at 1050 nm.