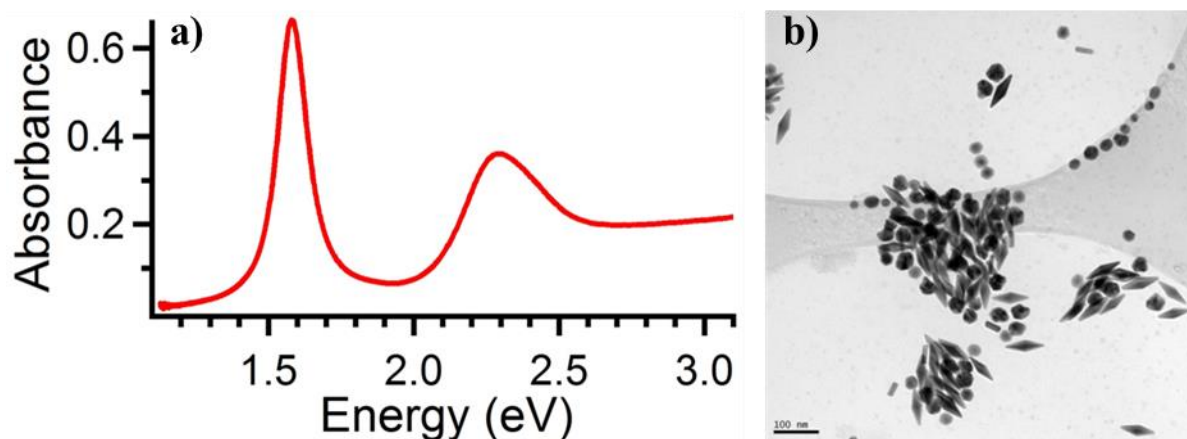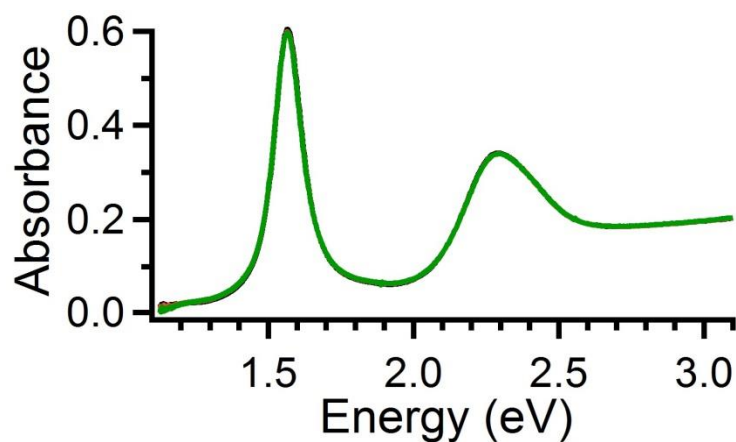**Synthesis and Characterization of Gold Bipyramid Nanoparticle Dimers**
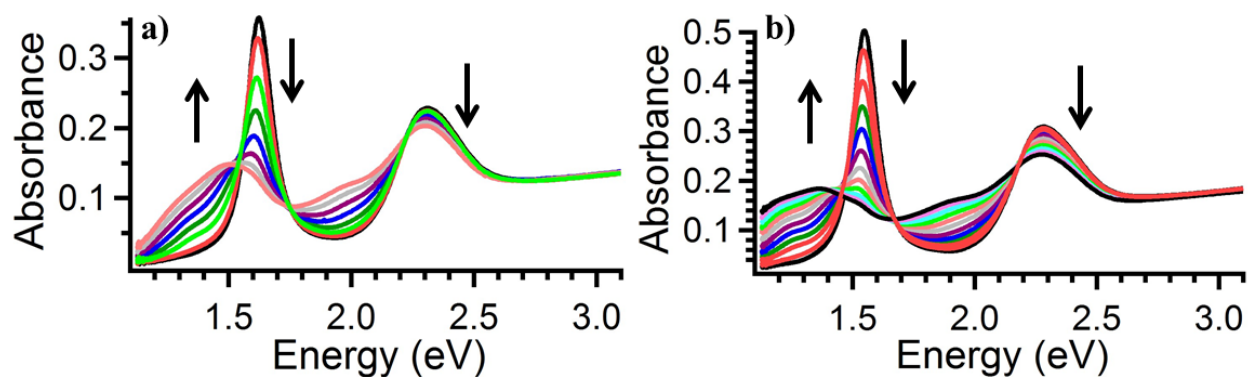
Edward W. Malachosky, Philippe Guyot-Sionnest

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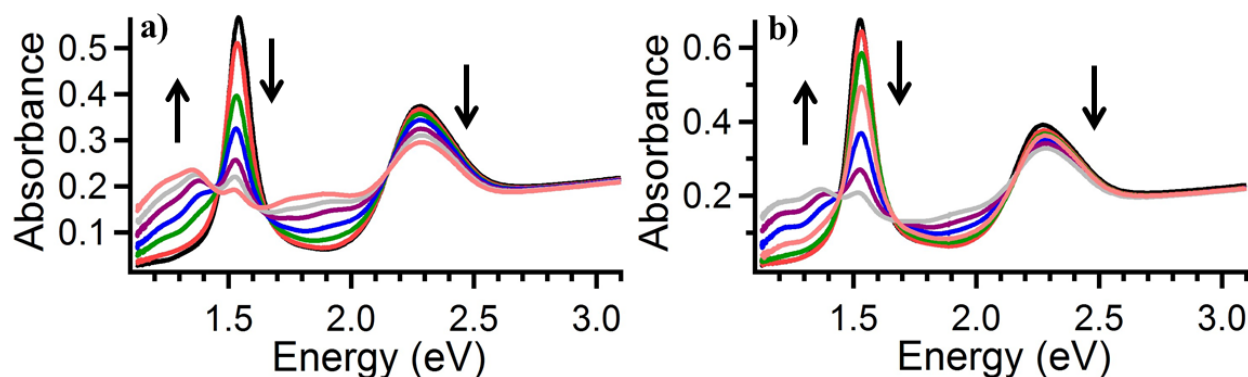
Figure SI1. a) UV/vis absorption spectrum of as synthesized AuBP colloid. b) Representative TEM image of the particles in a).

Figure SI2. UV/vis spectra of the reaction colloid monitored for an hour without the addition of a linker molecule. The lack of change in the spectra indicates that the reaction mixture is stable and the changes in the UV/vis spectra of the reaction solutions are caused by the linking molecules.
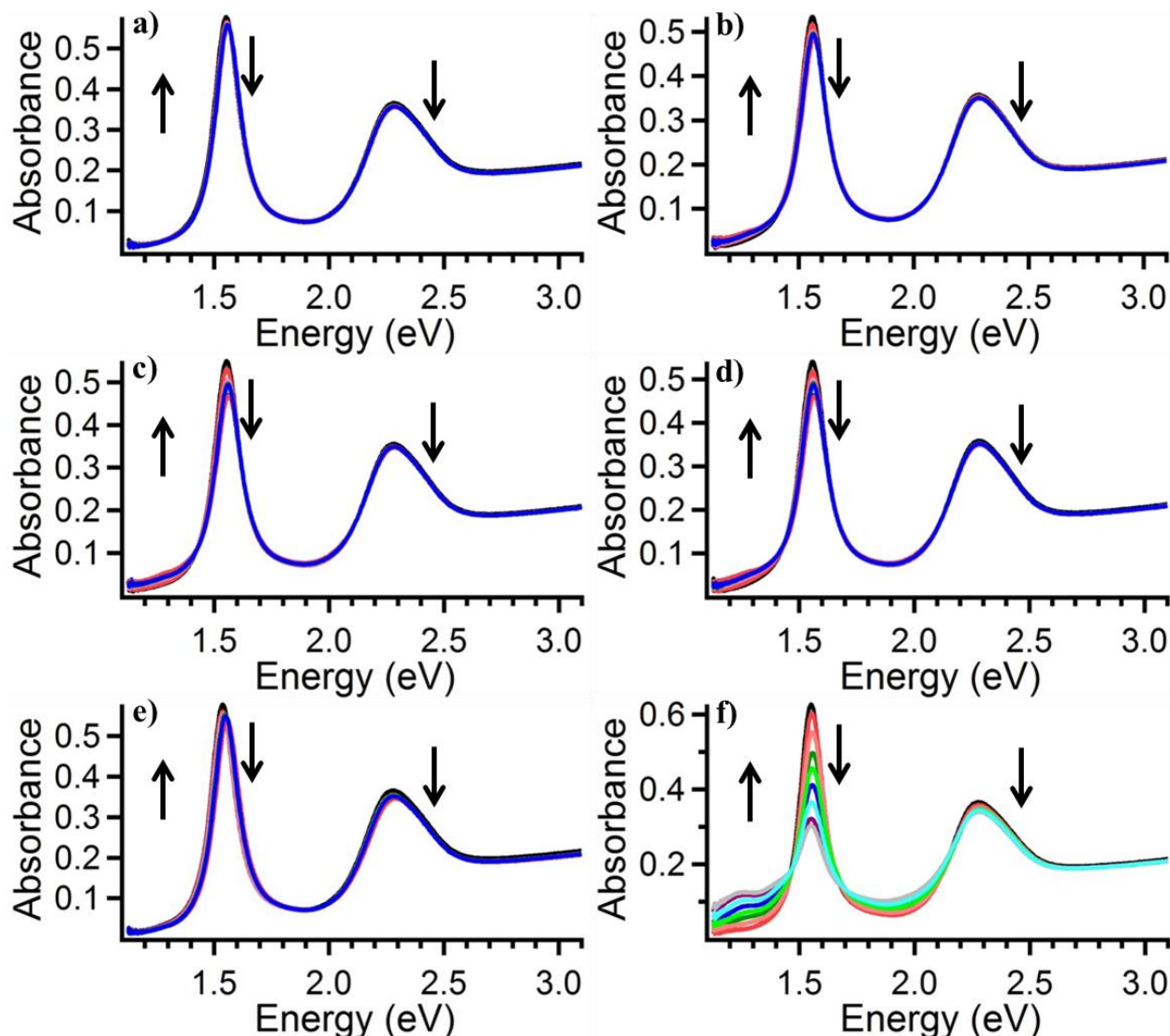
Figure SI3. Time resolved UV/vis spectra of early AuBP assembly reactions using two different stock colloid samples. The spectra exhibit very different shapes, even though the stock colloids were treated the same and the reaction mixtures were the same. The arrows indicate the how the peaks evolved with time.

Figure SI4. a) Representative time resolved UV/vis spectra of an assembly reaction using glutathione and the 2 mM CTAB stabilization solution. b) Representative time resolved UV/vis spectra of an assembly reaction using glutathione after the stabilization solution was changed to 1 mM CTAB/ 200 µM 5-BSA. The arrows indicate the spectral evolution with time.

Assembly reactions performed using different linking molecules:

To test the effect of the linking molecule on the assembly of the AuBPs, reactions were carried out under the following conditions: 3-MPA at pH=3 and pH=9, cysteamine at pH=3, mercaptoethanol at pH=3, tetra(ethylene glycol) dithiol at pH=7, and glutathione at pH=3. All of the reactions were monitored for an hour. As can be seen, only glutathione caused any definable spectral features to develop.

Figure SI5. Comparison of assembly reactions performed using different thiol linking molecules. a) 3-MPA at pH=9 b) Cysteamine at pH=3 c) 3-MPA at pH=3 d) Mercaptoethanol at pH=3 e) Tetra(ethylene glycol) dithiol at pH=7 f) Glutathione at pH=3. All reactions were monitored for one hour, and the arrows indicate how the spectra evolved with time. As can be seen, no other linker developed similar features to those observed with glutathione.
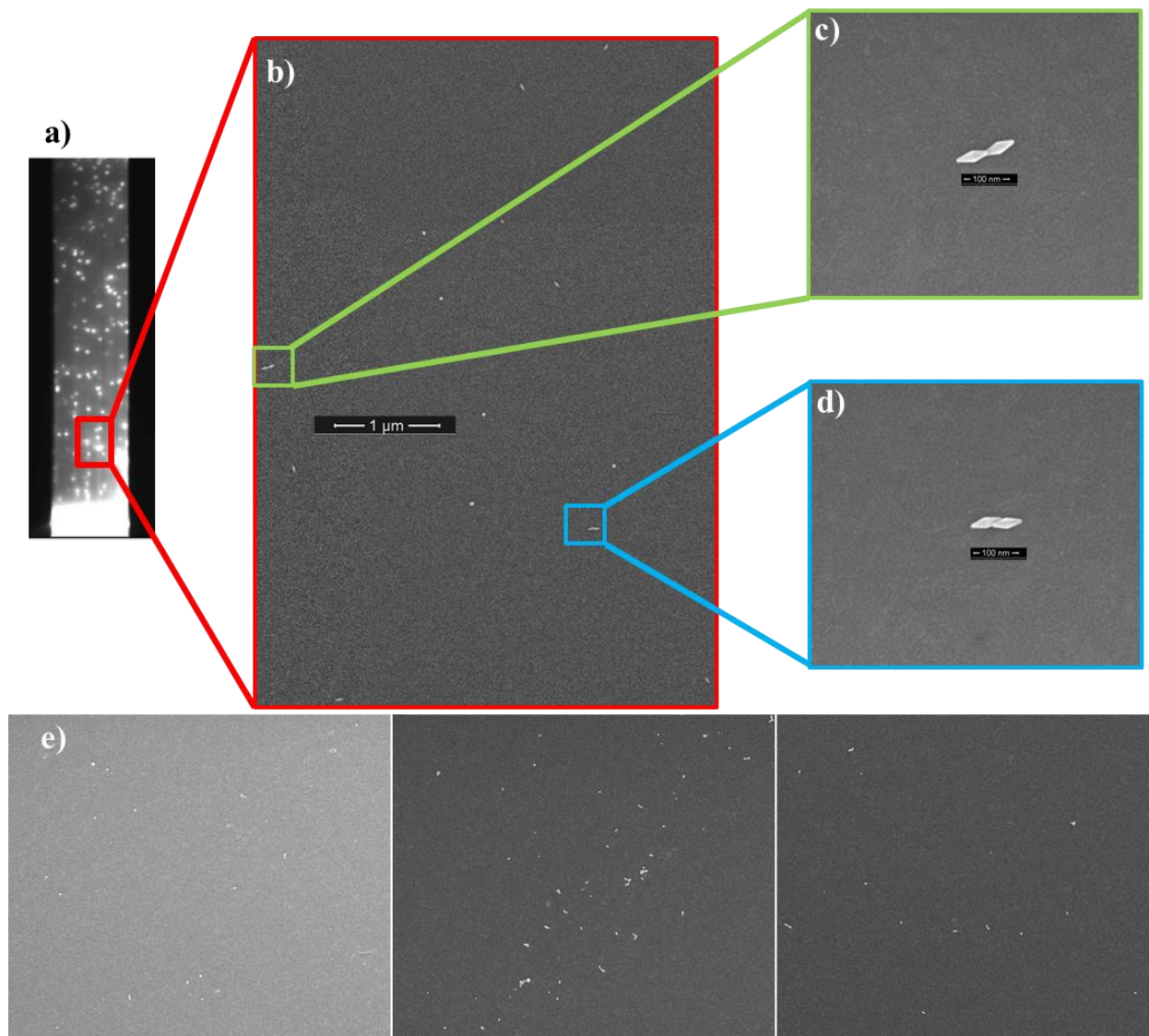
Theoretical Ratios for Dimer Structures:

If it is assumed that the linking molecule (explicitly, cysteine) does not selectively functionalize the AuBPs over the AuNSs, then the number of dimeric structures that would be observed would be governed by the statistics of amount of each type of particle. Building on the fact that a standard AuBP synthesis is only ~30% efficient,[1] the following ratios were developed:
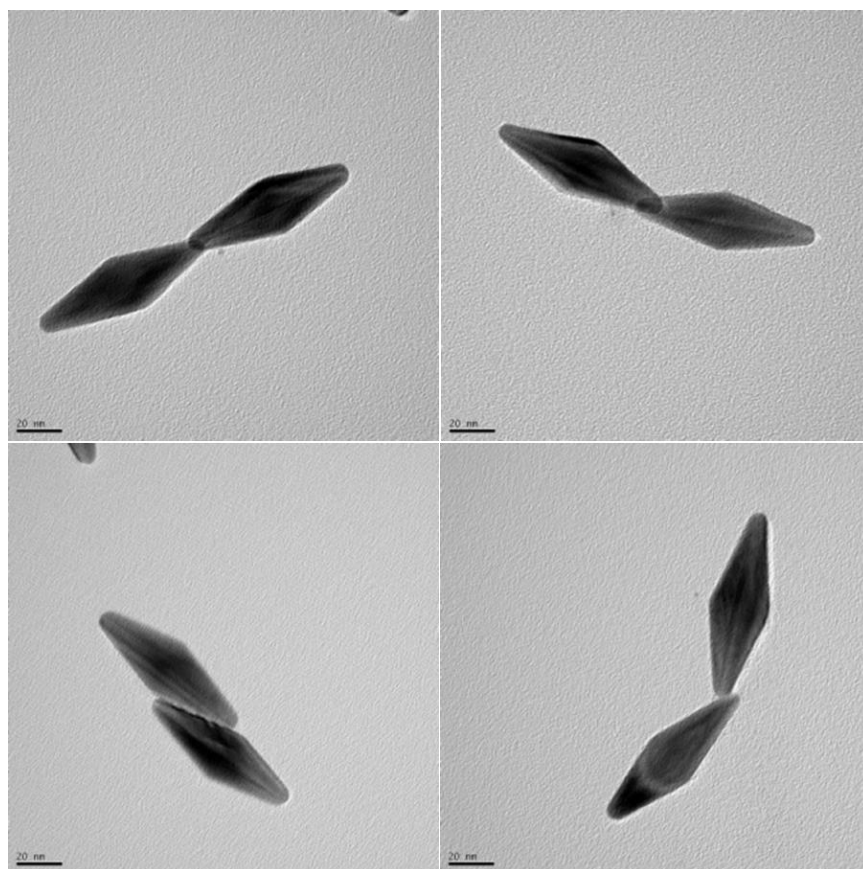
AuBP-AuBP	:	AuBP-AuNS	:	AuNS-AuNS
$0.30 * 0.30$	:	$(0.30 * 0.70) * 2$	:	$0.70 * 0.70$
0.09	:	0.42	:	0.49
1	:	4.7	:	5.4

Table SI1. Gold Bipyramid Dimer Type Analysis

Type	Bowtie	Longitudinal Edge-Edge	V-Shape
Counts	28	14	27
Ratio, per lone AuBP	0.035	0.018	0.034

Figure SI6. Outline of the DF and SEM matching for the representative bowtie dimer of Figure 2a and another, nearby longitudinal edge-edge dimer. a) The DF image collected from the CCD camera. The vertical distance is ~100 μm. From this image, a region of interest is identified for SEM mapping. b) The low resolution mapping of the region of interest outlined in a). Multiple SEM images of this region were taken and stitched together using the Gimp 2.8 software package. Then, the DF and SEM images were compared to match the scatterers and their plasmon resonances with their structures. c) and d) Full, high resolution SEM images of the bowtie dimer in Figure 2a and the nearby longitudinal edge-edge dimer, respectively, after the matching process and plasma cleaning. It is important to note that the only structures that scatter in the DF are the AuBPs, since we coated our lamp source in gold to decrease its emission for <550 nm. e) SEM images showing the results of our attempts to increase the number of AuBP dimers per SEM image of the substrate by multiple depositions. As can be seen, very few dimers are observable, while there are many trimers and other higher order aggregates present.
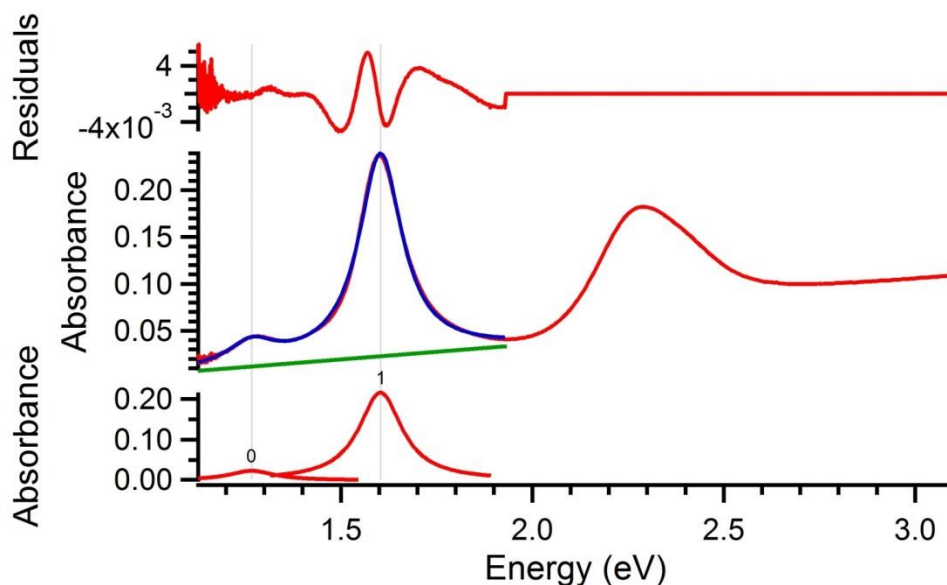
Figure SI7. Representative TEM images of AuBP dimer structures. The top two images clearly show particles with slight interparticle overlap, while the bottom two images clearly show dimers with a slight gap.

Peak Fitting Analysis Details:

All reaction spectra from Figures 1c and 1d in the text were fitted using Igor's Multipeak capability with a linear baseline for the regions of 1.1 eV to 1.93 eV. The results for the final time point of Figure 1d are shown in Figure SI8, and the locations of the peaks identified by Igor are listed in Table SI2 under 'Solution Peak Locations.'
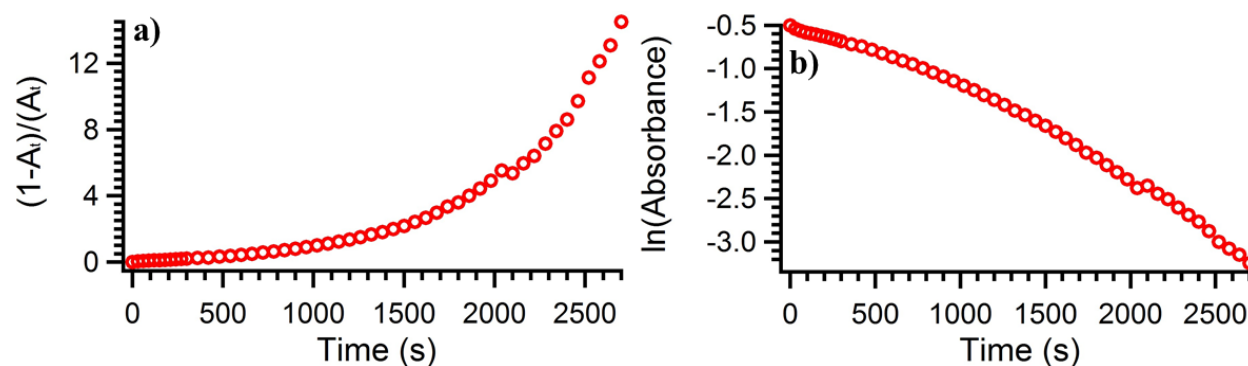

Figure SI8. The last time point UV/vis spectrum of Figure 1d. The region with energies less than 2.0 eV is fitted with Igor's Multipeak fit function using a linear baseline. The results are:

	Peak 0 (Bowtie)	Peak 1 (AuBP)
Position:	1.2668 eV	1.6034 eV
FWHM:	0.14305 eV	0.13701 eV
Area:	0.0052243	0.046394

Table SI2. AuBP Dimer Spectral Matching

Dimer Type	Average DF Resonance	Corrected Resonances	Solution Peak Locations
Bowtie	1.30 eV	1.28 eV	1.28 eV
Longitudinal Edge-Edge	1.40 eV	1.38 eV	1.43 eV
V-Shape	1.74 eV	1.72 eV	1.74 eV

Figure SI9. Attempted fittings of reaction kinetics. a) Second order, as described by Wang et al.[2] b) First order. The more linear relationship in b) indicates that the reaction is more closely exhibits first order, instead of second order, kinetics.

1. Liu, M.; Guyot-Sionnest, P. Mechanism of Silver(I)-Assisted Growth of Gold Nanorods and Bipyramids. *J. Phys. Chem. B* **2005**, *109*, 22192–22200.

2. Wang, Y.; Deprince III, A. E.; Gray, S. K.; Lin, X.-M.; Pelton, M. Solvent-Mediated End-to-End Assembly of Gold Nanorods. *J. Phys. Chem. Lett.* **2010**, *1*, 2692–2698.