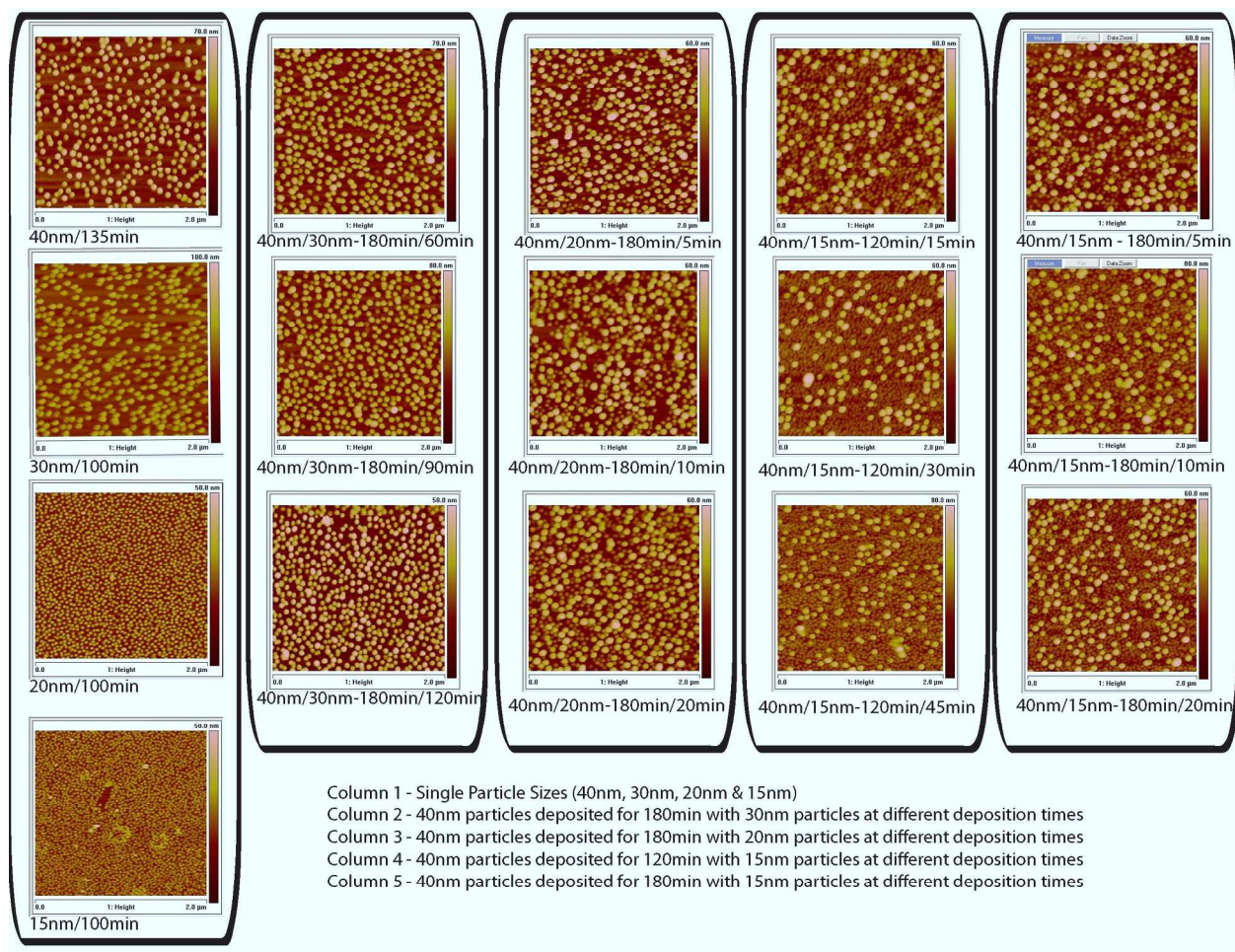
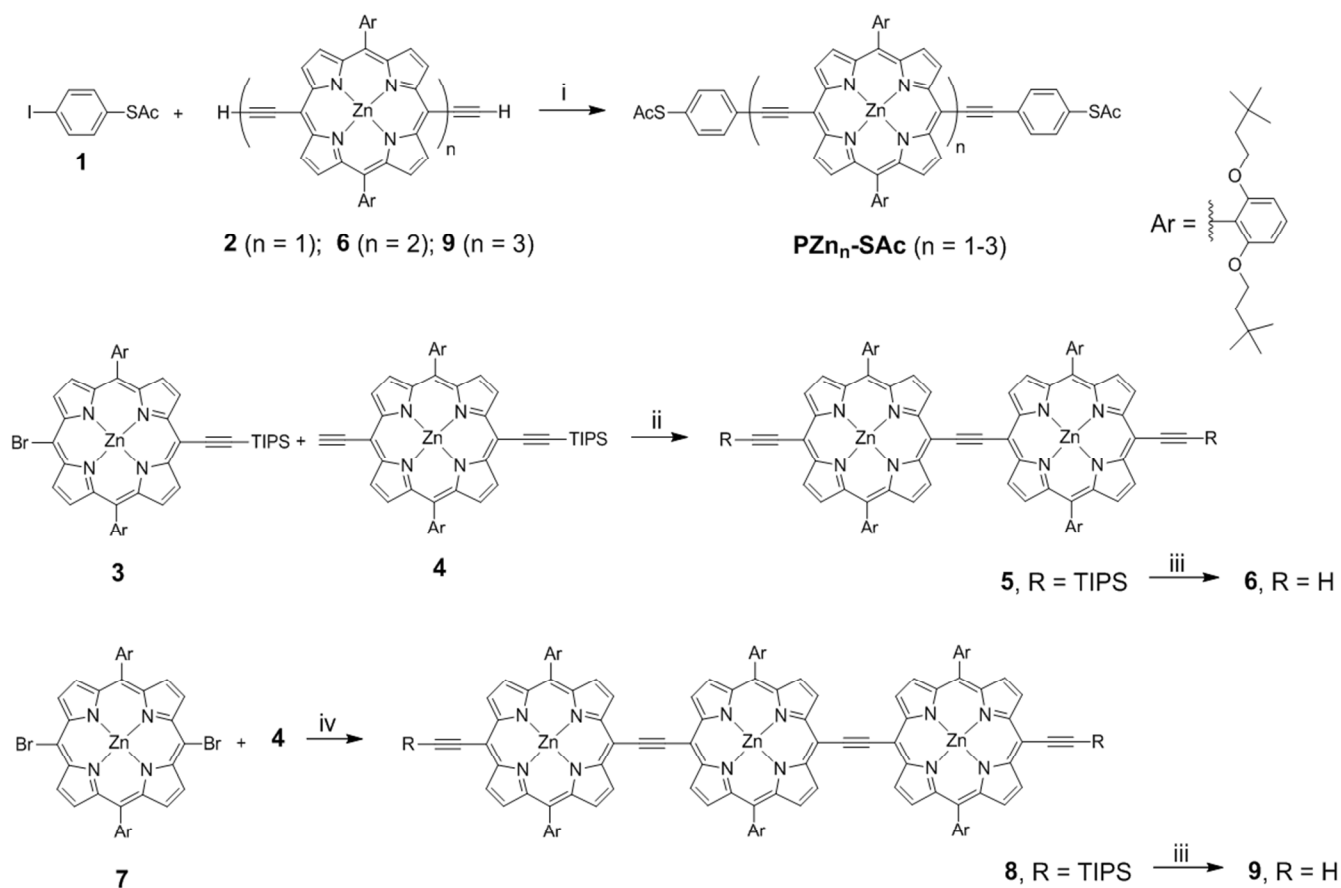


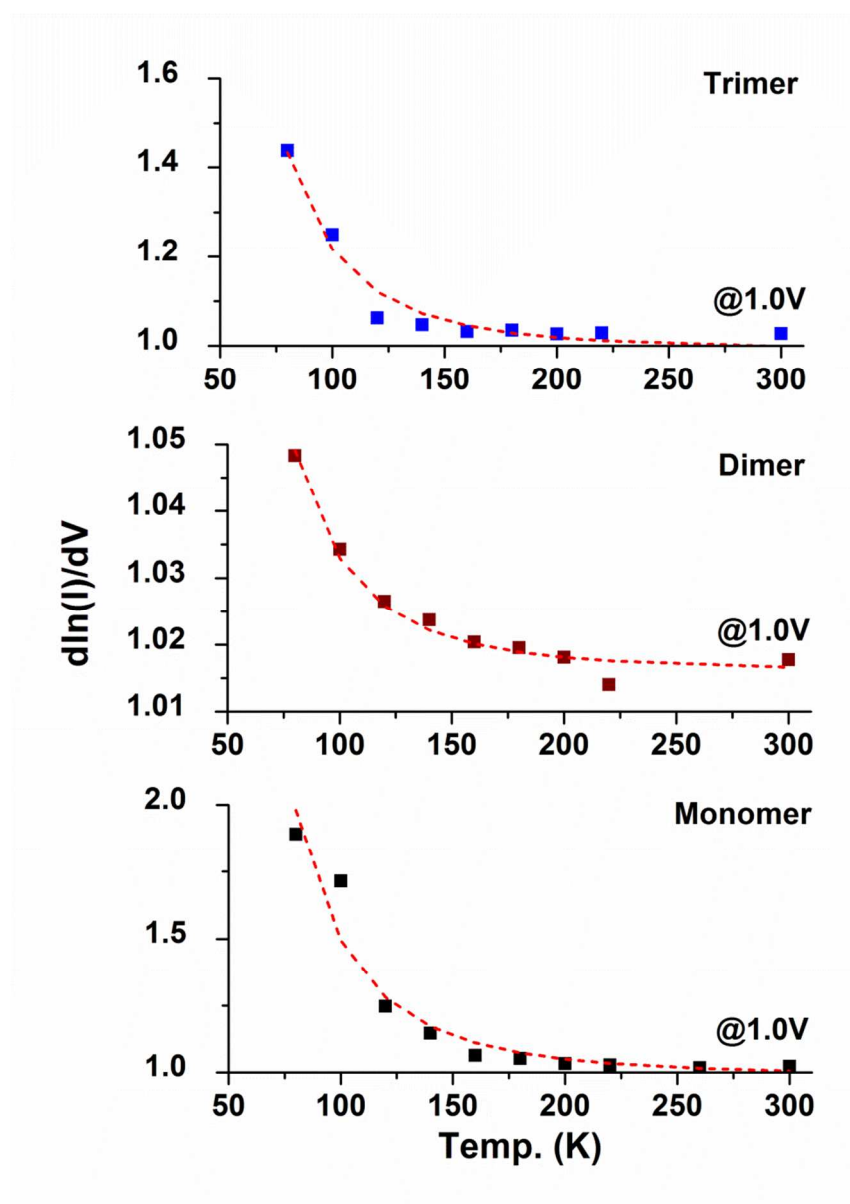
## Supplementary Figures:



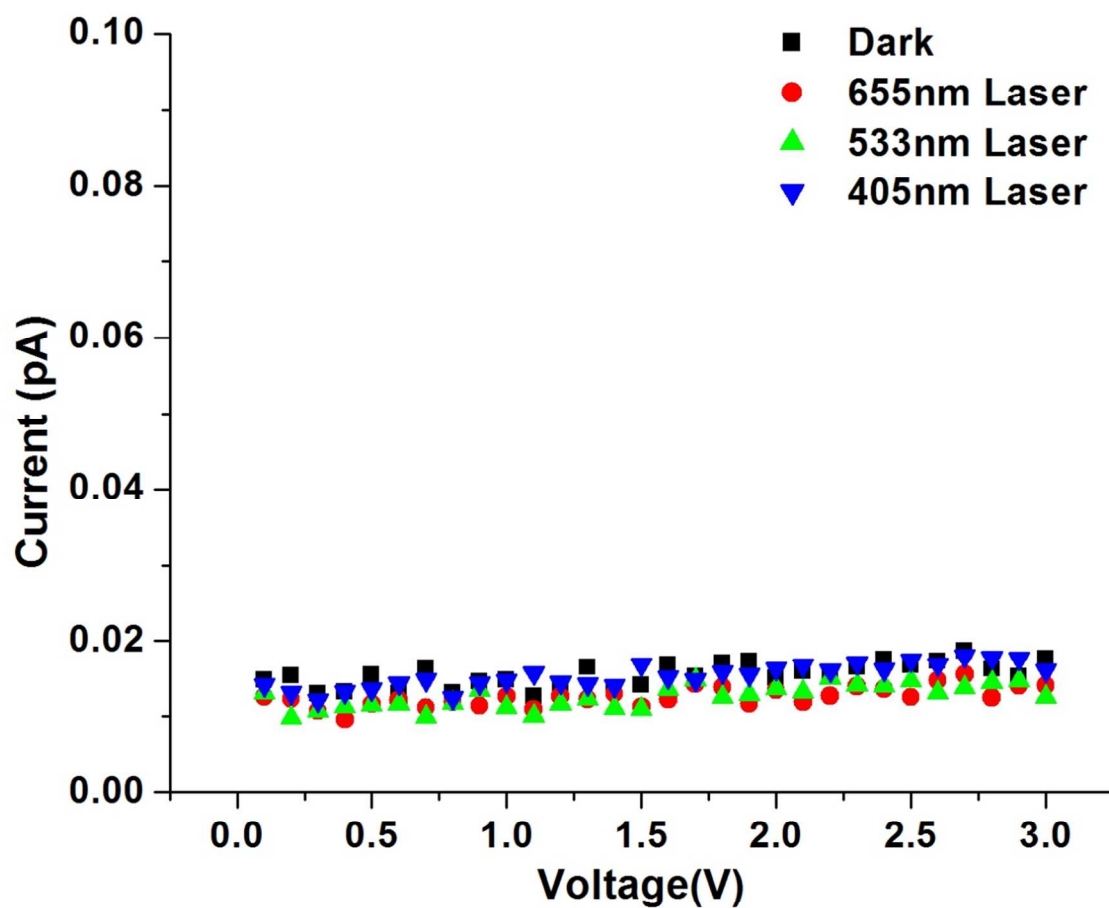
**Figure. S1.** Morphology of gold nanoparticle arrays as a function of processing parameters. The particle density and therefore average separation is controlled for arrays consisting of a single particle size ranging from 15 to 40 nm. Arrays with bimodal particle distributions were made with 40 nm particles combined with 30, 20 and 15 nm particles.



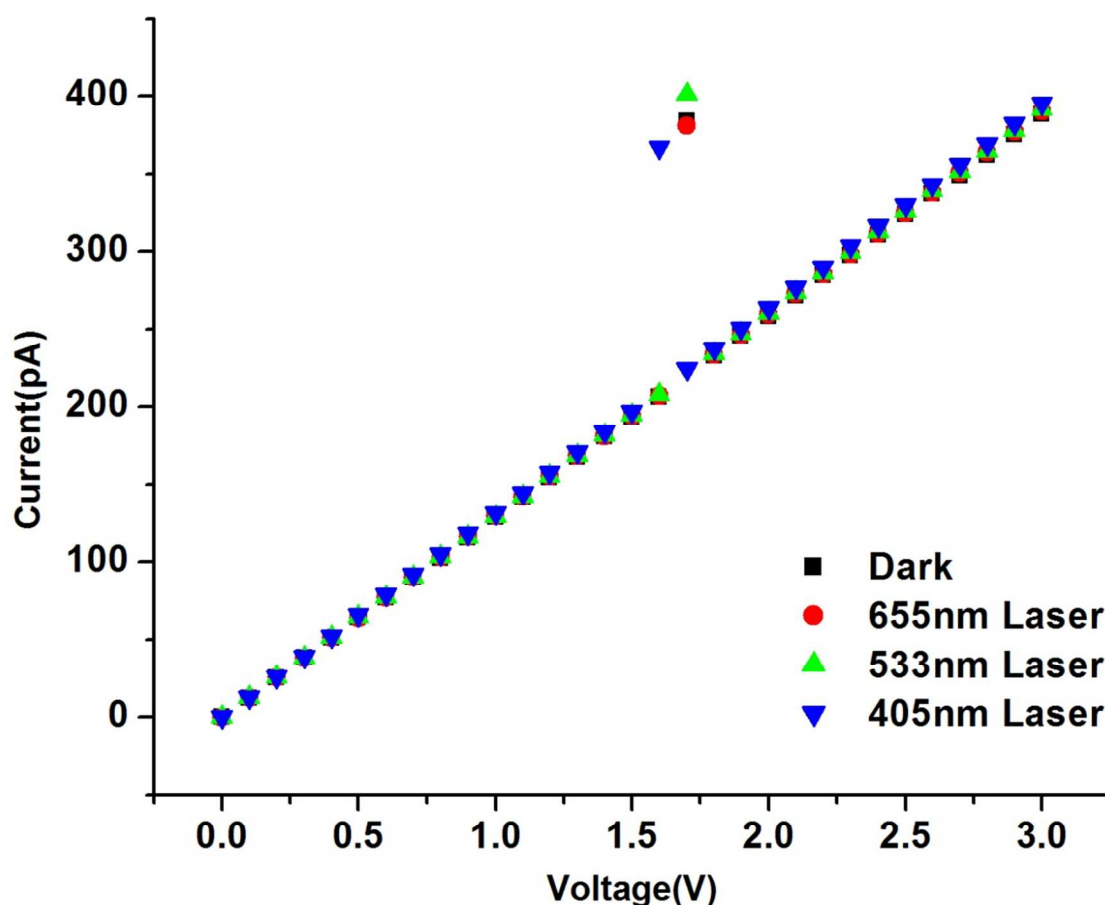
**Figure S2.** Synthesis of *S*-acetyl-protected dithiol-PZn<sub>n</sub> structures. (i) Pd(PPh<sub>3</sub>)<sub>4</sub>, THF/DIEA, 35-40 °C; (ii) Pd<sub>2</sub>dba<sub>3</sub>, P(*o*-tol)<sub>3</sub>, THF/Et<sub>3</sub>N, 60 °C; (iii) TBAF, THF, 0 °C; (iv) Pd<sub>2</sub>dba<sub>3</sub>, P(*o*-tol)<sub>3</sub>, CuI, *n*-Bu<sub>4</sub>NI, DMF/*i*-PrNH, 70 °C.



**Figure S3.** Differential analysis of the dark current transport mechanism for dithiol-PZn<sub>1</sub>-, dithiol-PZn<sub>2</sub>-, and dithiol-PZn<sub>3</sub>-linked devices. The squares are the data and the lines are fit of the thermally assisted tunneling mechanism. These are representative of all devices used in this study.



**Figure S4.** Transport properties of 30 nm nanoparticle array before molecular linker attachment. The current at all wavelengths is at the noise floor of the measurement system demonstrating that photo assisted tunneling does not occur between the particles, and multi photon excitation in the particles does not occur or cause transport.



**Figure S5.** A control study for transport mechanisms in the nanoparticle arrays. Here the transport properties of a 30 nm array linked with oligo(phenylene ethynylene) (OPE), 4,4'-(1,4-phenylenebis(ethyne-2,1-diyl))dibenzenethiol are compared. OPE is a conjugated conductive molecule that exhibits no optical absorption in the wavelengths used here and is not photoconductive. The thiol bonding to the particle is similar to that used with dithiol-PZn<sub>1</sub>, dithiol-PZn<sub>2</sub>, and dithiol-PZn<sub>3</sub>, thus ensuring a similar effect upon metal work function. The complete overlap of the properties at all wavelengths with the dark current demonstrates that the presence of a molecular linker does not facilitate photocurrent mechanisms. (The points off the line near 1.6 V result from instrument error on scaling)