Electronic Supplementary Information

Switching plasmon coupling through the formation of dimers from

polyaniline-coated gold nanospheres

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Fig. S1 Scanning electron microscopy images of the PGNS sample. The homodimers and oligomers consisting of more than two Au nanospheres are both present in the product. The average PANI shell thickness is 10 ± 2 nm. (a) At a low magnification. (b) At a high magnification.



Fig. S2 Correlation between the optical properties and geometrical characteristics of the individual Au nanostructures. (a,b) Dark-field scattering images of the Au nanosphere sample at a low and high magnification, respectively. (c) TEM image of the Au nanospheres taken from the same area as in (b). (d) Zoomed-in TEM image of the single Au nanosphere as indicated in (c). (e) Dark-field scattering spectrum recorded on the Au nanosphere shown in (d).



Fig. S3 Dielectric functions of PANI at the proton-doped and undoped states. (a) Real parts.(b) Imaginary parts.



Fig. S4 FDTD simulation of the switchable plasmonic response of a single PGNS monomer. The monomer has a 10-nm PANI shell thickness and is supported on a carbon film-coated TEM grid. (a) Schematic of a single PGNS denting into the carbon film on the TEM grid. The polarization of the incident light and its wavevector are represented with the orange and grey arrows, respectively. (b,c) Scattering spectra of the PGNS at different dent depths at the doped and undoped states, respectively. (d) Variations of the scattering peak wavelengths as functions of the dent depth at the doped and undoped states. The data points were extracted from the simulated scattering spectra shown in (b,c). (e) TEM image of a representative PGNS, whose PANI shell thickness is 10 ± 2 nm. (f) Measured and simulated scattering spectra of the PGNS shown in (e). The scattering spectra have been normalized against the scattering peak intensities at the undoped state for the measured and simulated spectra, respectively.



Fig. S5 Comparison of the measured and simulated scattering spectra of the homodimers. The homodimers have different gap distances and are at the doped or undoped states. (a) The gap distances in both experiment and simulation are 6.0 nm. (b) The gap distance in the experiment is 15.8 nm and that in the simulation is 16 nm. (c) The gap distances in both experiment and simulation are 0.5 nm. The measured PANI shell thickness is 10 ± 2 nm. It is 10 nm in the simulations. The scattering spectra have been normalized against the intensities of the stronger scattering peak at the undoped state for the measured and simulated spectra, respectively.



Fig. S6 Lorentzian fitting of the measured scattering spectra of the homodimer with a 2.2nm gap distance. The PANI shell thickness is 10 ± 2 nm. (a) At the doped state. (b) At the undoped state. The coefficients of determination for the spectra in (a) and (b) are 0.9991 and 0.9748, respectively.



Fig. S7 Effect of the PANI shell thickness on the switching of the plasmon coupling. (a–c) TEM images of the homodimers with measured gap distances of 0.5 nm and PANI shell thicknesses of 4 ± 1 nm, 10 ± 2 nm and 22 ± 1 nm, respectively. The insets in (a–c) are the zoomed-in TEM images in the gap regions. The scale bars in the insets are all 10 nm. (d) Measured scattering spectra of the homodimers at the doped and undoped states of PANI. The spectra of each dimer have been normalized against the intensity of the stronger scattering peak at the undoped state. The spectra from top to bottom were measured on the homodimers shown in (a–c), respectively.



Fig. S8 Plasmonic response of the homotrimers of the PGNSs in isosceles triangles with the same side length but different base lengths at the proton-doped and undoped states. (a) TEM image of the related homodimer with a 15.8-nm gap distance and a 10-nm shell thickness. (b–d) TEM images of the trimers with a 10-nm shell thickness and gradually enlarged vertex angles. The vertex angles are 46° , 60° , 122° , and the upper/lower gap distances, as indicated with the dashed lines, are 16.3 nm/15.0 nm, 16.2 nm/15.3 nm, 15.7 nm/15.4 nm, respectively. (e–h) Scattering spectra of the dimer and trimers shown in (a–d) at the proton-doped (green curves) and undoped (blue curves) states.