Supporting Information

Dark Plasmon Modes in Symmetric Gold Nanoparticle Dimers Illuminated by Focused Cylindrical Vector Beams

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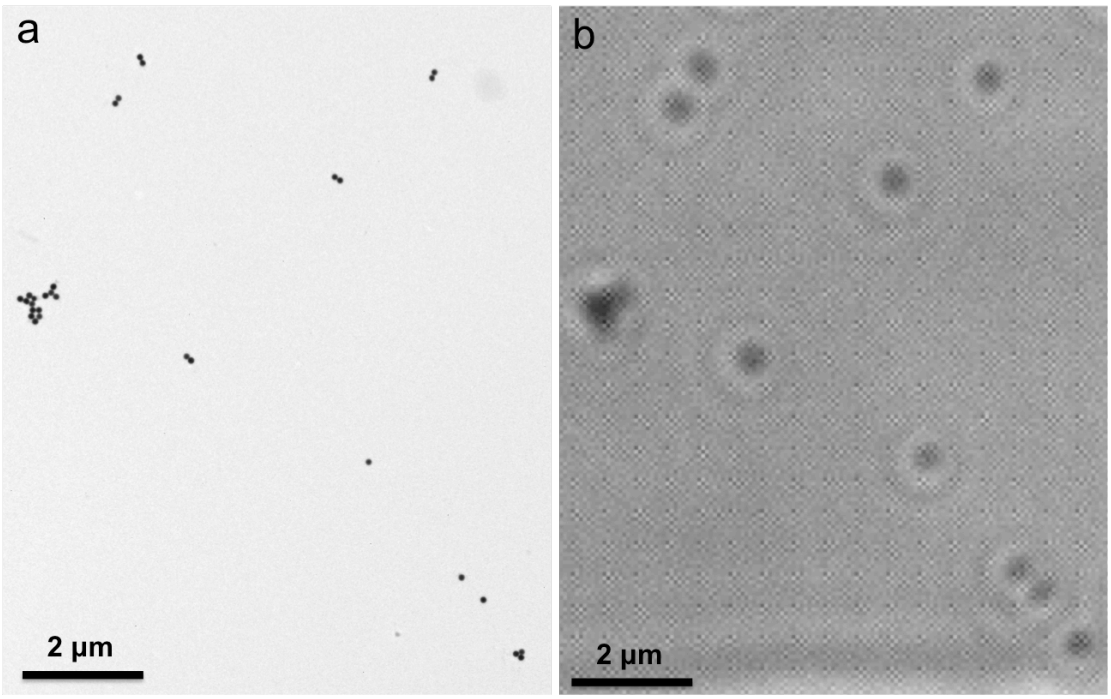


Figure S1. TEM (a) and optical microscope (b) images from the same area of the sample. We can readily conduct single particle spectroscopy measurements by using the EM finder grid. Their spatial correspondence and correlation allows obtaining the structure and scattering spectra of individual AuNP dimers. However, neither measurement is limited to dimer nanostructures. To avoid any possibility of scattering from neighbor particles that could affect the spectra measurement, the dimers we chose to measure are well separated (~5 µm).

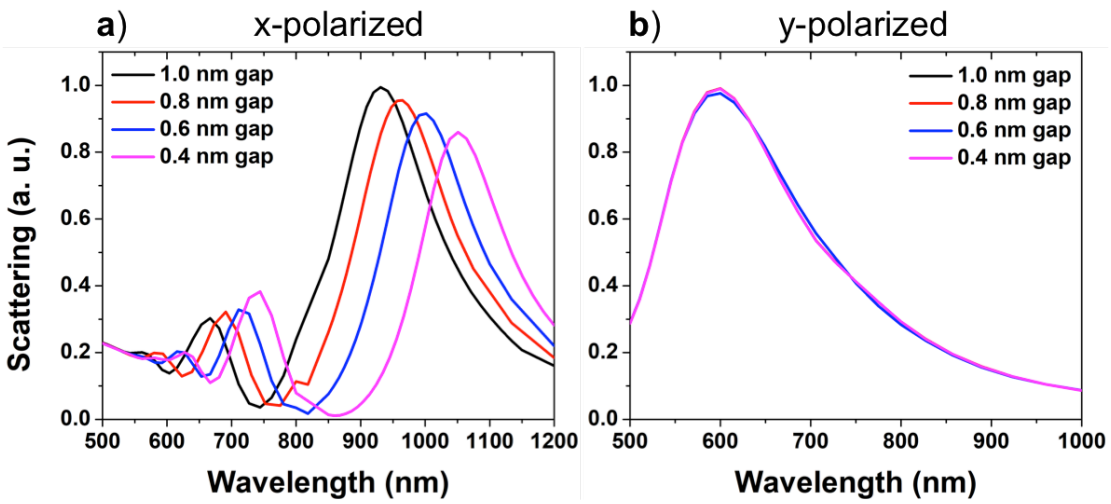


Figure S2. Simulated scattering spectra excited by linearly polarized beams. (**a**) The scattering spectra are obtained for polarization of the incident field parallel to the dimer axis (x-polarized), and (**b**) scattering spectra obtained for illuminating beams linearly polarized perpendicular to the dimer axis (y-polarized).

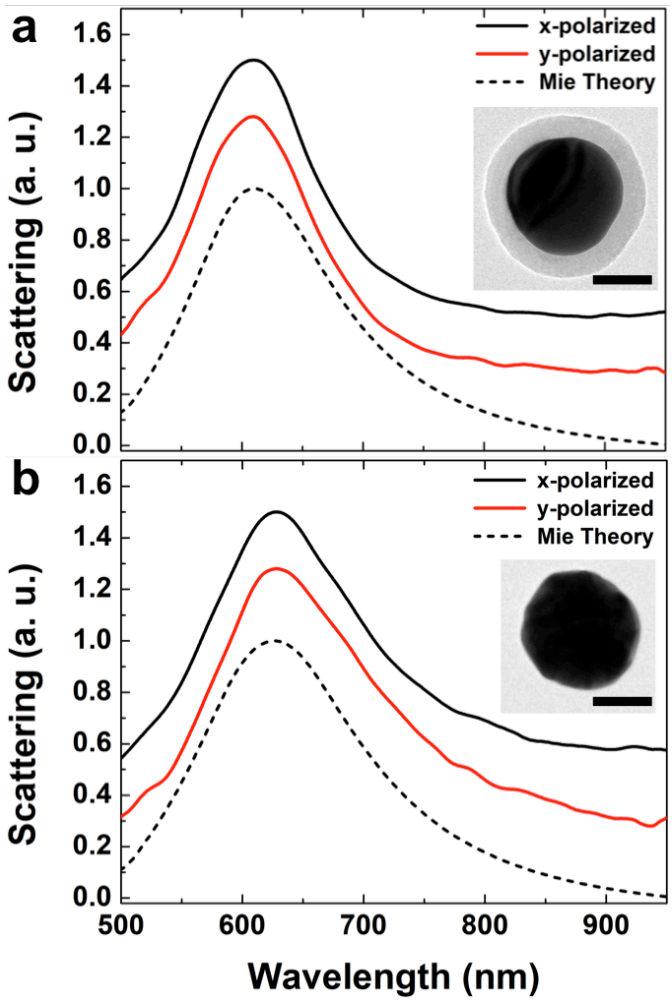


Figure S3. Scattering spectra of individual nanoparticles excited by a focused linearly polarized beam. (a) AuNP@SiO_2, the AuNP core is 105 nm in diameter, and the LSPR is peaked at 610 nm. (**b**) AuNP, 108 nm in diameter, and the LSPR is at 628 nm. Black solid curves are the scattering spectra excited by light polarized along the x-axis direction. Red solid curves are the spectra excited by y-polarized light. Black dashed curves are the scattering spectra calculated by Mie theory. The Mie scattering spectra were calculated using the values of particle size and SiO_2 shell thickness measured from TEM images. The effective refractive index n of the environment used for Au@SiO_2 is 1.47 (between SiO_2 (n = 1.45) and immersion oil (n = 1.51)), and for AuNP is 1.51 (refractive index of immersion oil). TEM images in the insets are the same nanoparticles that gave rise to the scattering spectra obtained with focused linearly polarized optical beams. The scale bars in the TEM images are 50 nm.

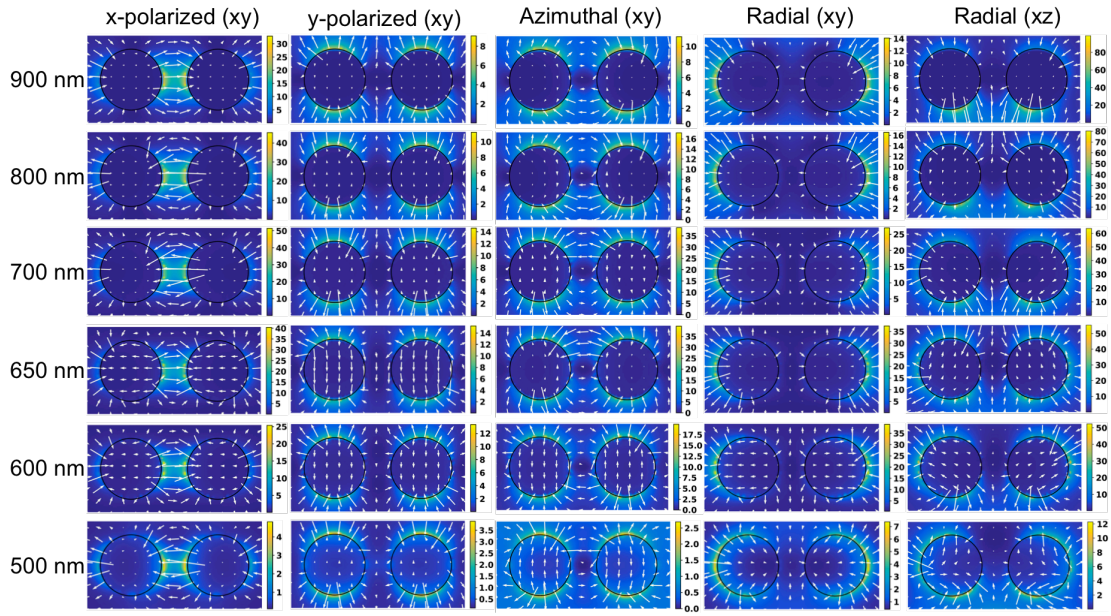


Figure S4. Near field intensity distribution for x-polarized, y-polarized, azimuthally and radially polarized light. The simulated AuNP diameter is 100 nm with 40 nm gap distance. The 1st to 4th columns are the xy plane (focal plane) and the 5th column is the xz plane. Six wavelengths of 900 nm, 800 nm, 700 nm, 650 nm, 600 nm, and 500 nm were selected for each polarization.

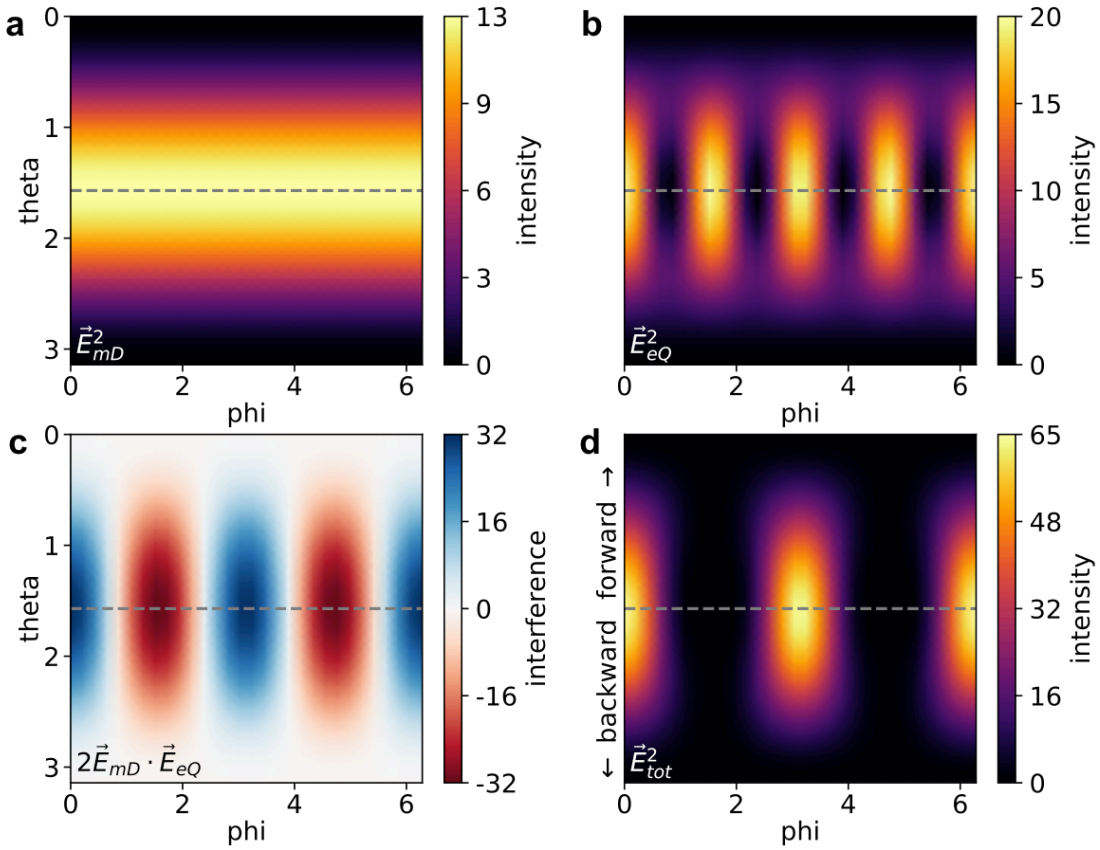


Figure S5. Angular scattering distributions obtained from FDTD simulations of the AuNP dimer (with 40 nm gap) for azimuthally polarized beam illumination. (**a**) Angular scattering of the z-oriented magnetic dipole mode. (**b**) Angular scattering of the electric quadrupole mode. (**c**) Angular scattering of the interference term between magnetic dipole and electric quadrupole modes. Red denotes destructive interference and blue denotes constructive interference. (**d**) Total angular scattering of the AuNP dimer. The interference between the magnetic dipole and electric quadrupole modes creates an interference pattern of similar intensity both in the forward and backward direction.

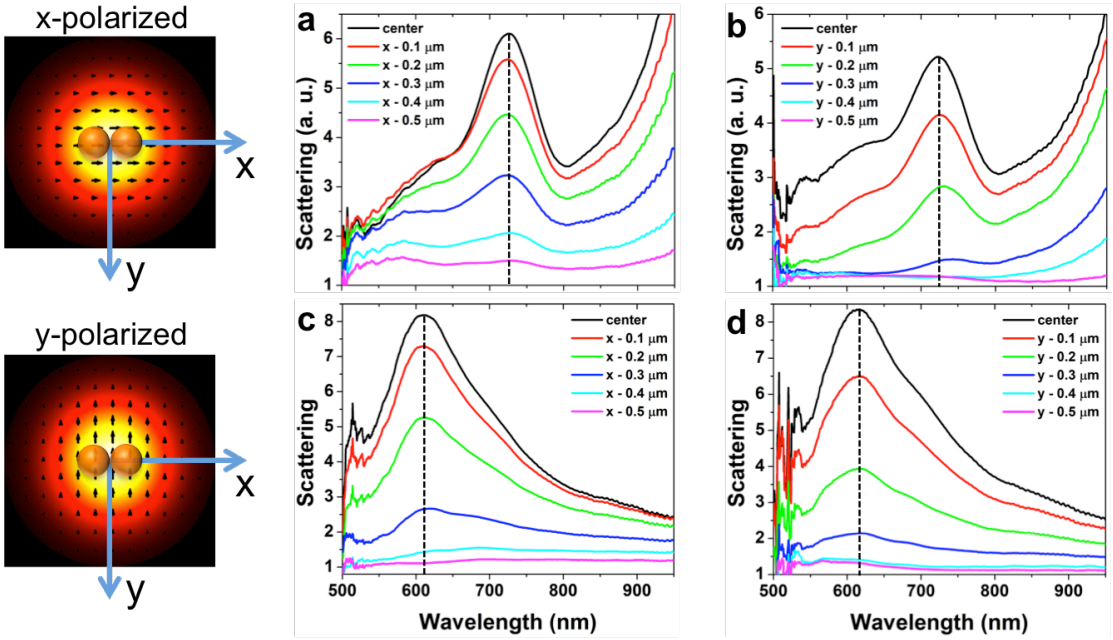


Figure S6. AuNP dimer (sub-nanometer gap) spectra at different x- and y-positions with respect to the beam axis. (**a**)-(**b**) Scattering spectra for x-polarized beam (parallel to the dimer axis) while moving the AuNP dimer in the x- (**a**) and y- (**b**) directions. (**c**)-(**d**) Scattering spectra for y-polarized beam (perpendicular to the dimer axis) while repositioning the AuNP dimer along the x- (**c**) and y- (**d**) directions. The left panels schematically indicate the directions of the spatial shifts along the x- and y-directions. The black curves in (a)-(d) are the spectra obtained when the AuNP dimer is centered on the optical beam axis. The black dashed lines indicate the plasmon resonance peak wavelengths, which don't change while spatially shifting the AuNP dimer away from the center of the incident beam. The particle and beam size shown in the left panels are from the simulation indicating their spatial overlap.

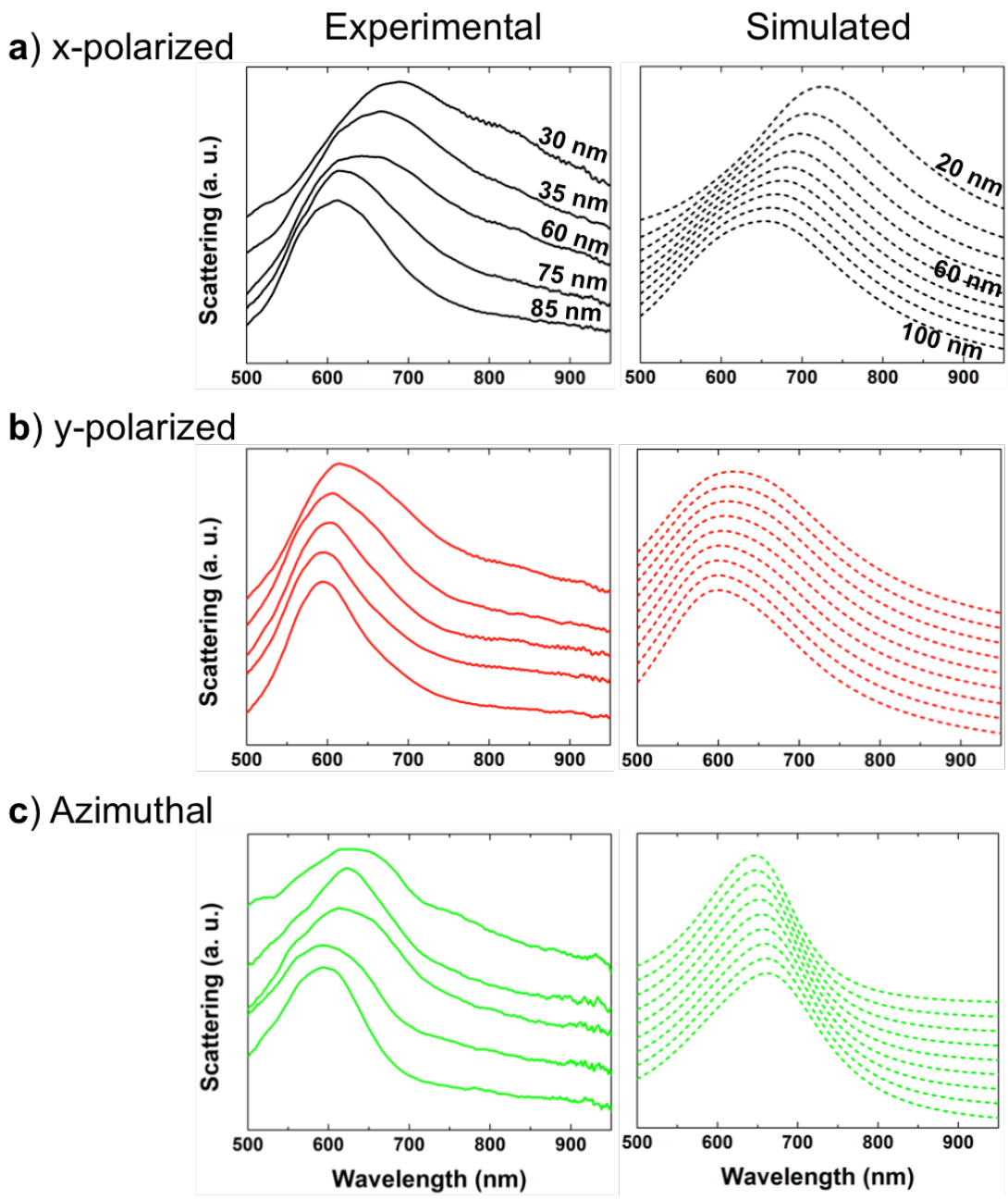


Figure S7. Experimental and simulated spectra of AuNP dimers with different gaps excited by (a) x-polarized, (b) y-polarized, and (c) azimuthally polarized light. From top to bottom, the gaps are 30 nm, 35 nm, 60 nm, 75 nm, and 85 nm in the experimental spectra, and are from 20 to 100 nm, with step size of 10 nm in the simulated spectra. The experimental and simulated spectra are in good agreement.

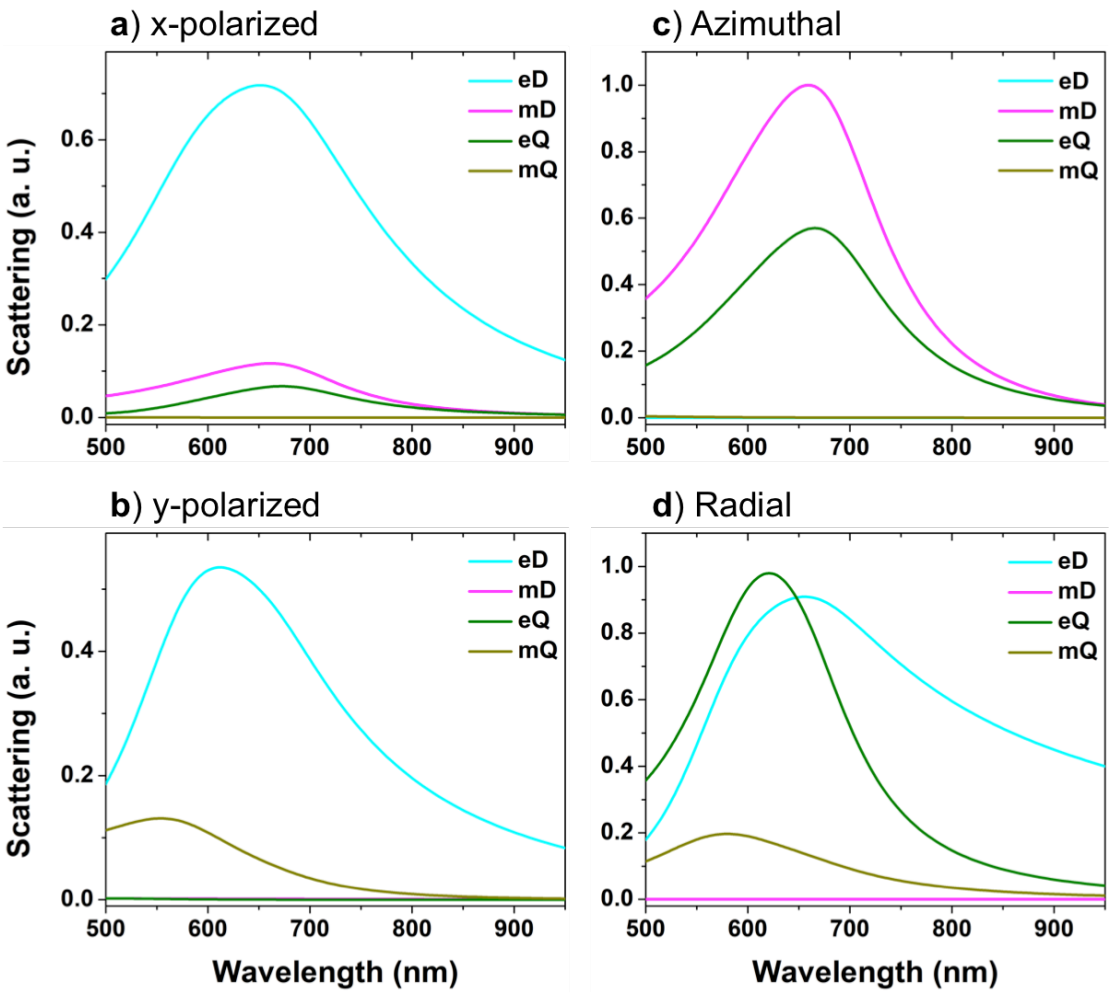
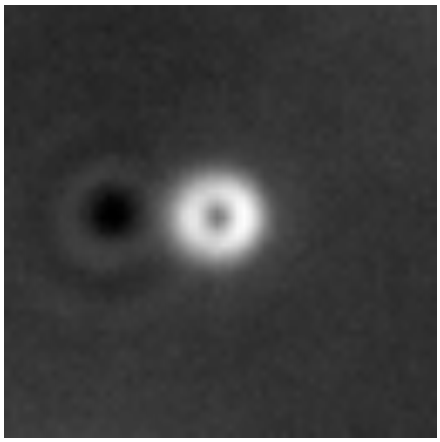


Figure S8. Expansion of the FDTD scattering amplitudes into electric and magnetic multipolar modes for a 100 nm gap AuNP dimer. The simulated results are for (**a**) x-polarized, (**b**) y-polarized, (**c**) azimuthally polarized, and (**d**) radially polarized beam excitation. Compared to the 40 nm gap AuNP dimer (Figure 3d), the scattering spectra associated with the eD and eQ modes are more overlapped for radial beam illumination, resulting in more symmetric spectra (Figure 7c, bottom spectra).



Video S1. The AuNP dimer shifted from left side to the right side of the doughnut shaped vector beams with 200 nm step size. During the shift, the AuNP dimer is from left side, left arc, center, right arc, and right side of the vector beams.