Supporting Information

Plasmonic Trimers for Dual-Frequency Surface-Enhanced Two-dimensional Infrared Spectroscopy

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1. Experimental details and referencing

The 2DIR measurements were performed with a fully-automated dual-frequency 2DIR spectrometer with heterodyned detection. The spectrometer consists of a Ti:sapphire laser which produces 1.5 W power at 1 kHz repetition rate and 80 fs pulse duration. These pulses propagate through a dual optical parametric amplifier and difference frequency generation units to produce the desired mid-IR color. The resulting mid-IR pulses are 150 fs in duration at the sample. The 2DIR spectra were obtained by scanning along τ. The typical scan consisted of 500 points with a 0.7 μm step size and 400 accumulations per point. The power of each laser pulse was reduced by an order of magnitude, and the probe was further reduced by another order of magnitude, when measuring any sample on the trimer array to prevent any light-induced degradation of the antennas. When measuring the off-gold reference, the power of each laser was increased an order or magnitude for both 10 nm and 190 nm films to facilitate a stronger signal. The difference in laser power was then accounted for when calculating the raw signal enhancement.

Our previous work showed that the concentration of the guest azNHS molecules in the sample decreased with the decrease of the film's thickness. The 190 nm film has an azNHS concentration of 2.35 M in the polystyrene (PS) matrix, whereas the 10 nm film is only 0.4 M. Therefore, when referencing to the thicker film for the cross-peak measurements (and CNC for the linear measurements), the change in concentration was also accounted for.

2. Supplementary figures

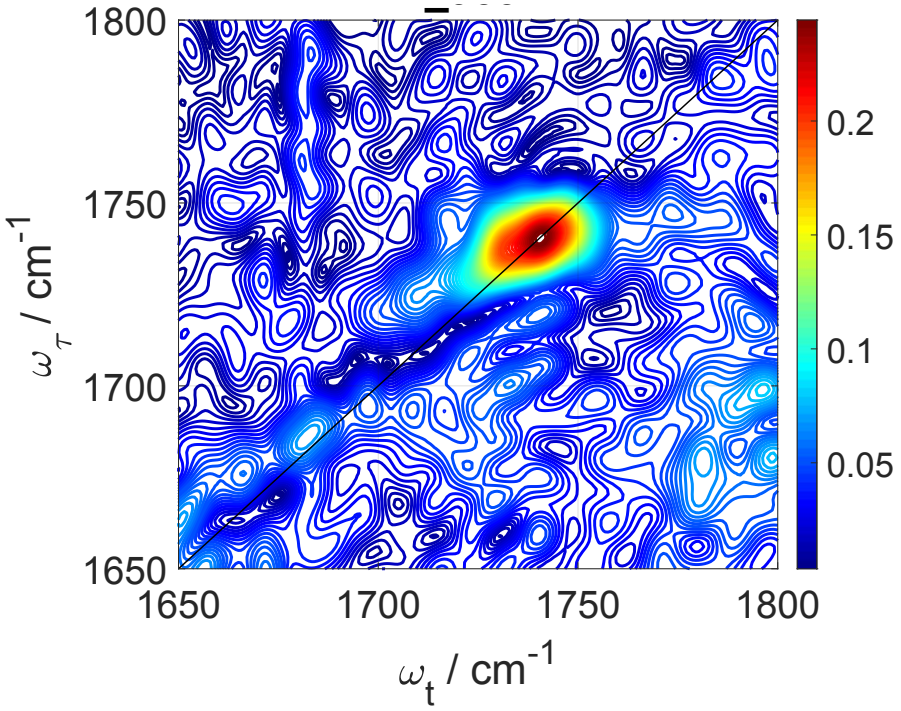

Figure S1. 2DIR diagonal magnitude spectrum for the 10 nm azNHS/PS film measured off the trimers with parallel polarization. The measurement was performed with a 10-fold increase in the laser power of each beam as compared to the measurements on the trimer array.