Supporting information

Local Protonation Control using Plasmonic Activation

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All SERS and TERS measurements are performed with an experimental setup described previously.\textsuperscript{1} Laser radiation is focused using an oil immersion microscope objective (40X, 1.35NA, Olympus). The scattered signal is collected with the same objective and passes through a dichroic mirror and notch filter before it enters the spectrometer (Acton Advanced SP2750 A, SI GmbH, Germany). The control experiments under continuous flow of argon and temperature dependent studies are performed in a Biocell (JPK, Germany).

SERS active silver island film were prepared by evaporation of silver on cleaned glass plate according to the literature.\textsuperscript{2} A drop of 5x10\textsuperscript{-3} M ethanolic solution of 4-MPY was put on SERS substrate and then dried and washed with ethanol to remove any unattached molecules on the surface.

For the TERS measurements the synthesis of gold nanoplates on cleaned glass substrate was performed according to a previously described method.\textsuperscript{3} A self-assembled monolayer of 4-MPY was prepared by immersing the gold nanoplate substrate for 22 hours in a 5x10\textsuperscript{-3} M ethanolic solution and washed with ethanol before the measurement. For the TERS measurement silver coated non-contact AFM tips (ND-MDT, NSG10) were used. 20 nm of silver was evaporated onto the tips following Ref 2.

References: