

Utilizing far field effects of Tip-enhanced Raman spectroscopy to detect a monolayer of diblock copolymer colloidal reverse micelles

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The following files are available free of charge. The following supplementary details are available free of charge.

- Raman spectra for KBr substrate used for background subtraction.
- Schematic of experimental set-up for the various Raman techniques
- Volume resolution limits of conventional Raman
- Raman spectra for complexated P2VP in PS-P2VP micelles
- Comparative table of measured intensity of PS mode

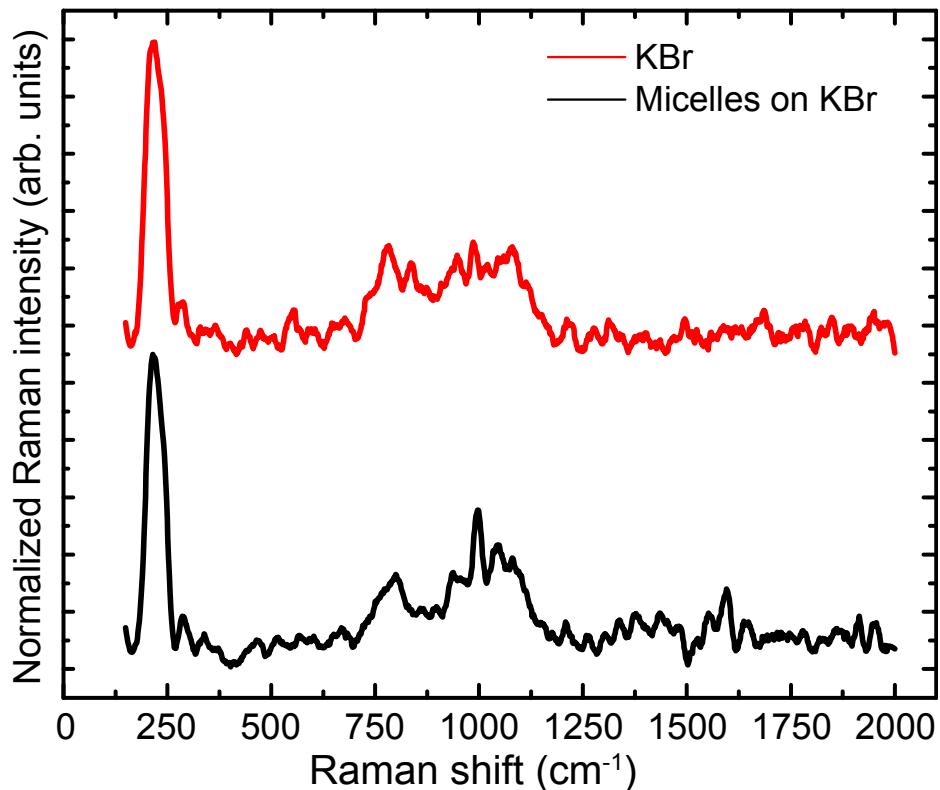


Figure SI-1 Raman spectra of KBr for background subtraction and unsubtracted P4824 empty micelles coated KBr.

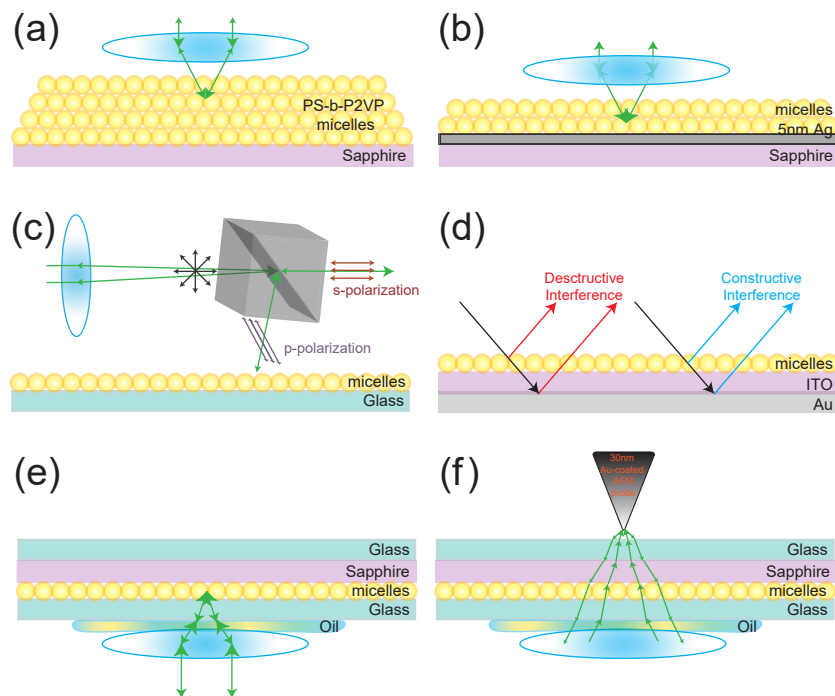


Figure SI-2 Configurations of various Raman set-ups for (a) normal Raman of thick micelles on Sapphire; (b) SERS of multilayer micelles on 5nm-Ag-coated Sapphire; (c) Polarized Raman with Glenn-Taylor prism of monolayer micelles; (d) IERS of monolayer micelles; (e) Inverted Raman of monolayer micelles and (f) Unconventional TERS of monolayer micelles

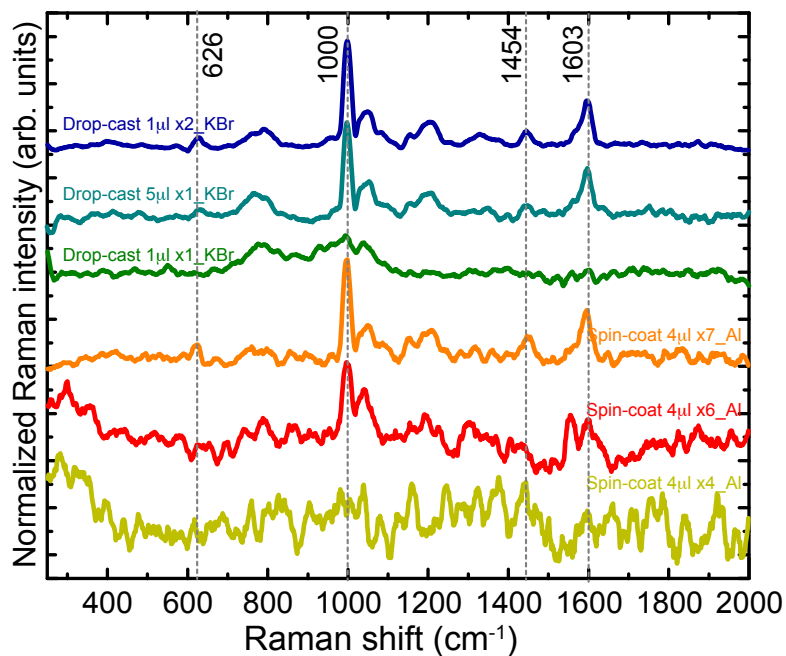


Figure SI-3 Raman spectra of different amounts of micelles on KBr (dropcast) and Al (spin-coated) substrates

Table SI-1 Table of signal intensity of the PS ring breathing at 1000 cm^{-1} obtained from the spectra for each technique.

Technique	Intensity of PS ring breathing mode (counts)	Accumulation time (s)	Accumulation normalized intensity (counts/s)	Enhancement vs NR	Thickness of polymer film (nm)	Accumulation and volume normalized intensity (counts/s nm)	Enhancement vs NR
uc-TARS	3406196	1000	3406.20	502.39	20	170.31	3014.33
SERS	2261	100	22.61	3.33	40	0.57	10.00
Inverted Raman	58098	200	290.49	42.85	20	14.52	257.07
IERS	2273	140	16.24	2.39	20	0.81	14.37
Inverted Raman @60	4489	30	149.63	22.07	20	7.48	132.42
Inverted Raman @45	2423	30	80.77	11.91	20	4.04	71.47
Normal Raman	678	100	6.78	1.00	120	0.06	1.00

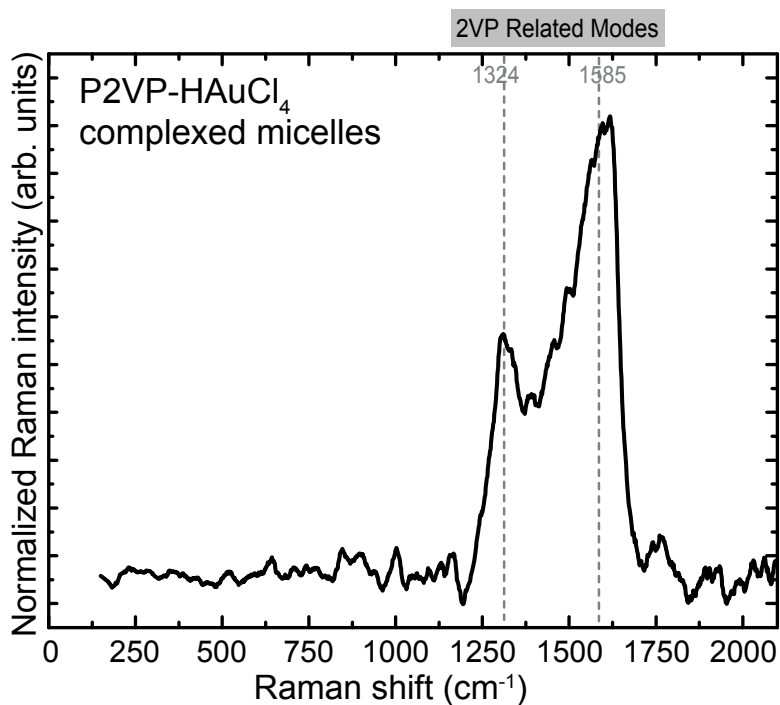


Figure SI-4 Raman spectra of micelles with complexation of P2VP with Au salt, showing the characteristic peaks associated with metal complexation on pyridine.