

Supplementary information

Interfacial processes studied by the coupling of electrochemistry at the polarised liquid-liquid interface with *in-situ* confocal Raman spectroscopy

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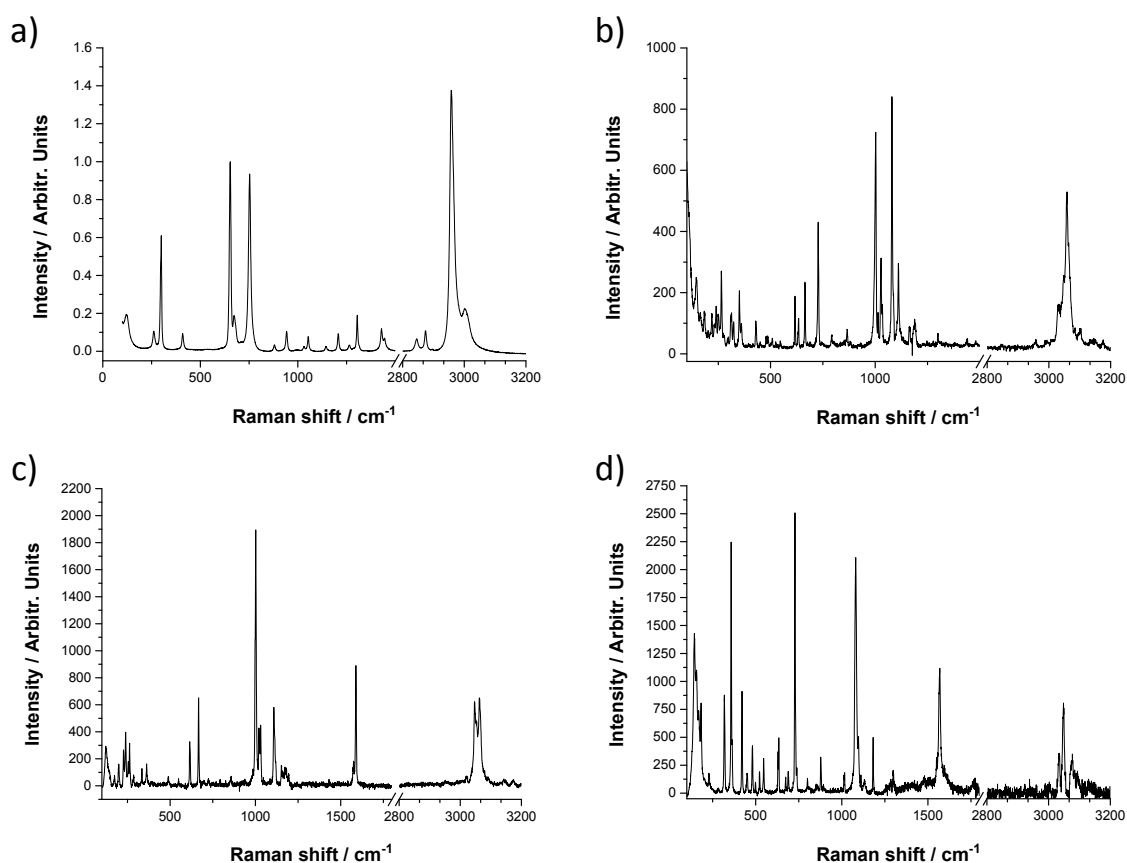


Figure S11. Raman spectra recorded for a) DCE, b) BTPPA⁺TPBCl⁻, c) BTPPA⁺Cl⁻ and d) K⁺TPBCl⁻.

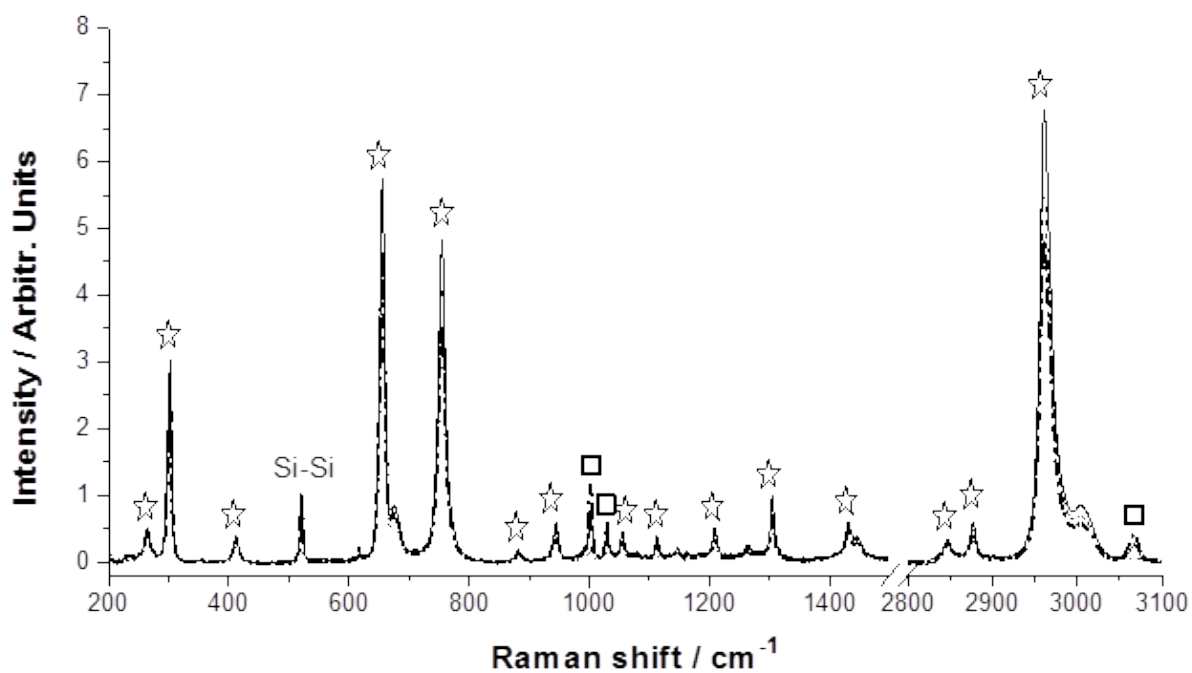


Figure SI2. Full Raman spectra recorded at the μ ITIES (5 mM NaCl aqueous phase and 10 mM BTPPA⁺TPBCl⁻ in organic phase) at open circuit potential (dashed line), under negative polarization potential -300 mV (solid line) and -800 mV (dotted line). Raman bands marked with (□) were assigned to BTPPA⁺ and with (★) to DCE.

Table S11. Summary of the bands observed in the different Raman spectra

Molecule of interest	Raman shift frequency ¹ cm ⁻¹	Peak assignment ¹	Description ¹
CTA⁺	3000 – 2840	-CH ₂ - and -CH ₃ stretching	Strong and characteristic bands
	2962 ± 10	-CH ₃ Antisymmetric stretching	Strong intensity and characteristic frequencies
	2926	-CH ₂ - Antisymmetric stretching	Strong in Raman
	2872 ± 10	-CH ₃ symmetric stretching	Strong intensity and characteristic frequencies
	2853	-CH ₂ - Symmetric stretching	Often overlapped with CH ₃ in anti-symmetrical region
	1470 – 1440	-CH ₃ Antisymmetric bending	Medium intensity
	1470 – 1340	CH ₂ and CH ₃ bending	Not necessarily visible in Raman spectra
	1465	Scissoring (bending) mode	
	1305 – 1295	-(CH ₂) _n - in phase twisting mode	Medium – strong intensity in Raman
BTPPA⁺	3100 – 3000	Aromatic ring in C-H stretching region	
	1600 – 1000	Five aryl C-H bonds (in aromatic)	
	1500 – 1141	P=N	
	1130 – 1090	P-(Ph) ₃	Weak in Raman
	1010 – 990	Aromatic rings	Very strong in Raman
	1000 – 700	C – H bending	
TPBCl⁻	3070 – 3030	C-H of substituted benzenes	One strong band
	1620 – 1585	Mono- and disubstitued benzene	The two quadrant stretch components give rise to two bands. When benzene is substituent with Cl the bands will occur at lower limit.
	1590 – 1565		
	1083	Aryl-Cl in chlorobenzene	For phenyl group on para this

			band is seen in the 1130–1190 cm ⁻¹ region. From m to s in Raman
	420 – 390	Mono and parasubstitued benzenes	Very weak Raman band
DCE	3030 ²	-CH ₂ antisymmetric stretching	
	2987 ²	-CH ₃ symmetric stretching	
	730 – 710 ²	Cl-(CH ₂) _n -Cl stretching mode of the trans conformer	
	657 ²	CH ₃ -CH ₂ -Cl stretching mode of the gauche conformer	

1. D. Lin-Vien, N. B. Colthup, W. G. Fateley, and J. G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, London, 1991.
2. M. D. Young, N. C. Borjemscaia, and B. D. Wladkowski, *J. Chem. Educ.*, 2005, **82**, 912.