

Supplementary information:

Phase transitions of ionic liquid self-assembled monolayers on Au

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Supporting information

Results

SERS of MDMIBr

The Raman spectrum of MDMIBr corresponds to the bands previously reported for pure compounds or physically adsorbed on metal (Figure S1). The assignation of these bands has been reported in the literature for butylmethylimidazolium¹ and ethylmethylimidazolium², which correlates well with the Raman spectrum measured on the monolayer. SERS studies of methylimidazole or methylimidazolium molecules adsorbed on metal surfaces have been reported in the literature³. However, the SERS spectrum has not been reported previously for MDMIBr.

Figures

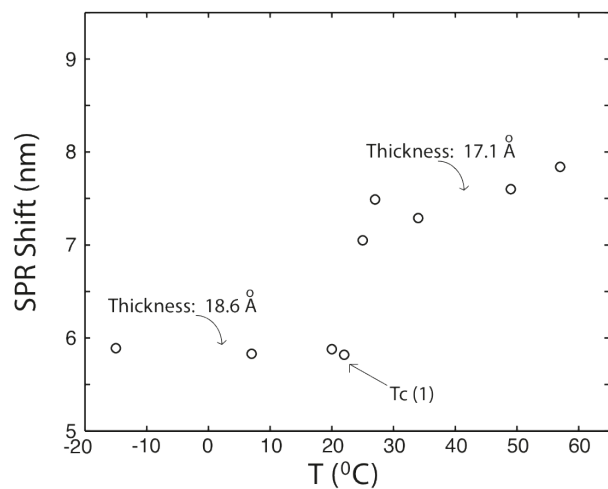


Fig. S1. Temperature dependent SPR shift during monolayer formation of MDMIBr on Au. The thickness was measured with ellipsometry at 4 °C and 40 °C.

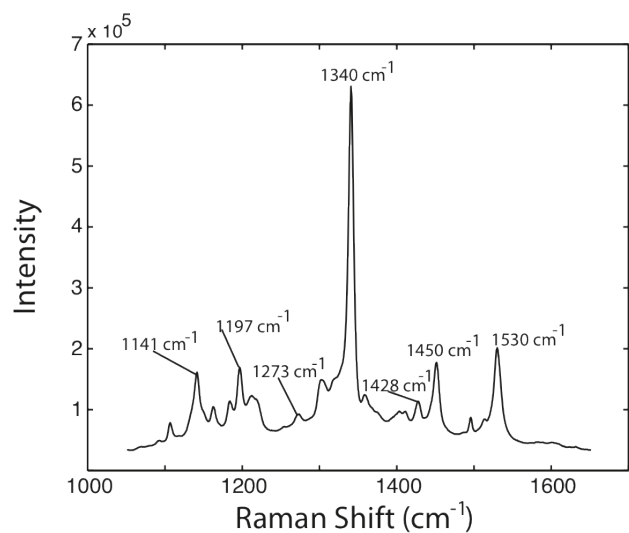


Fig. S2. SERS spectrum of MDMIBr monolayer on Au.

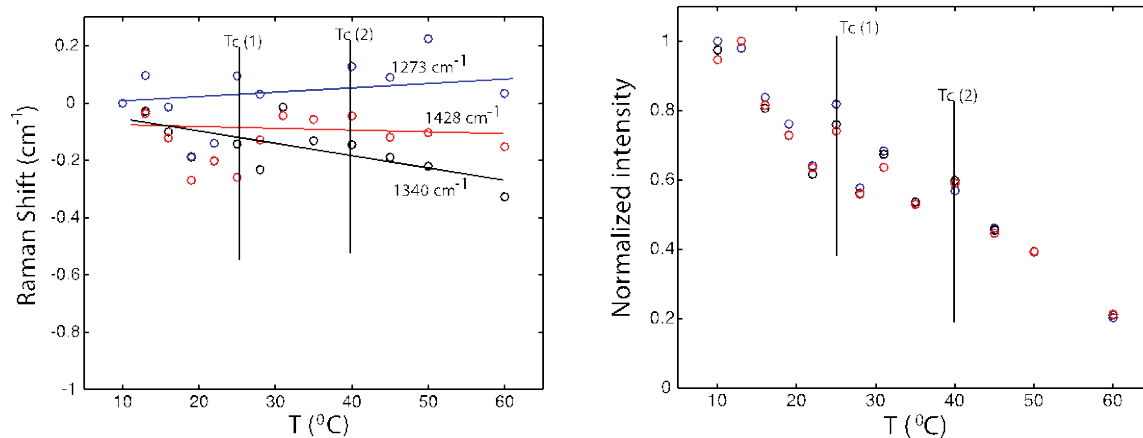


Figure S3. Left) Temperature dependent Raman shift for IL monolayers prepared at 40 °C. Right) Temperature dependent Raman intensity for IL monolayers prepared at 40 °C. The Raman bands are associated to the acidic C-H vibration of imidazolium (blue, 1273 cm⁻¹), imidazolium ring vibration (black, 1340 cm⁻¹) and to the methyl of the methylimidazolium group (red, 1428 cm⁻¹).

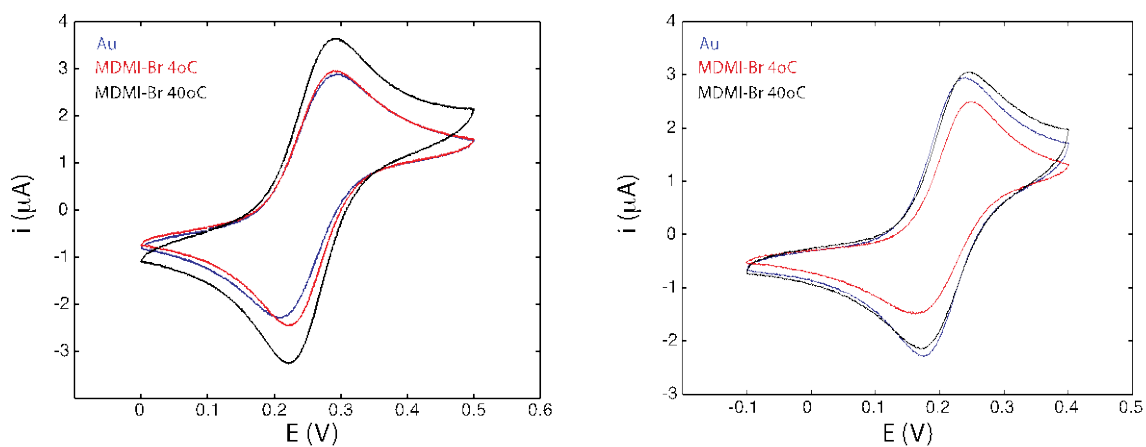


Figure S4. Cyclic voltammograms of: left) 1 mM Fe(CN)₆⁴⁻, right) 1 mM alpha-methylferrocene methanol. The bare gold electrode (blue), MDMI-Br deposited at 4 °C (red) and MDMI-Br deposited at 40 °C (black) were analyzed at a scan rate of 50 mV/s.

Table S1. Potential difference (mV) for $\text{Fe}(\text{CN})_6^{4-}$ and FcEtOH

Scan rate (mV/s)	$E_a - E_c (\text{Fe}(\text{CN})_6^{4-})$			$E_a - E_c (\text{FcEtOH})$		
	Au	MDMIBr 4°C	MDMIBr 40°C	Au	MDMIBr 4°C	MDMIBr 40°C
1	78.5 ± 1.8	79.5 ± 1.4	71.4 ± 1.9	75.3 ± 1.7	81 ± 3	78 ± 3
5	70.4 ± 1.7	69.0 ± 2.3	64.8 ± 2.3	65.3 ± 0.5	78 ± 9	70 ± 4
10	70.9 ± 1.7	69.4 ± 2.8	66.1 ± 3.0	64.3 ± 0.7	80 ± 13	69 ± 4
50	81 ± 7	81 ± 13	75 ± 4	64.3 ± 0.7	98 ± 31	76 ± 8
100	91 ± 8	86 ± 12	79 ± 4	68.7 ± 1.5	108 ± 36	84 ± 10
500	139 ± 12	131 ± 26	121 ± 9	96.9 ± 1.2	138 ± 28	129 ± 20

Table S2. Average potential (mV) for $\text{Fe}(\text{CN})_6^{4-}$ and FcEtOH

	$(\text{Fe}(\text{CN})_6^{4-})$			(FcEtOH)		
	Au	MDMIBr 4°C	MDMIBr 40°C	Au	MDMIBr 4°C	MDMIBr 40°C
Anodic	299 ± 13	302 ± 15	298 ± 10	243 ± 7	258 ± 21	251 ± 12
Cathodic	211 ± 12	216 ± 9	218 ± 10	170 ± 5	159 ± 13	166 ± 10

References

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2. Y. Umebayashi, T. Fujimori, T. Sukizaki, M. Asada, K. Fujii, R. Kanzaki and S. Ishiguro, *J. Phys. Chem. A*, 2005, **109**, 8976.
3. D. A. Carter, J. E. Pemberton and K. J. Woelfel, *J. Phys. Chem. B*, 1998, **102**, 9870; V. O. Santos, M. B. Alves, M. S. Carvalho, P. A. Z. Suarez and J. C. Rubim, *J. Phys. Chem. B*, 2006, **110**, 20379; J. C. Rubim, F. A. Trindade, M. A. Gelesky, R. F. Aroca and J. Dupont, *J. Phys. Chem. C*, 2008, **112**, 19670; C. R. R. Brandao, L. A. F. Costa, H. S. Breyer and J. C. Rubim, *Electrochem. Commun.*, 2009, **11**, 1846.