

## Supporting information

### **Probing double layer structure of Au (111)-BMIPF<sub>6</sub> ionic liquid interface from potential-dependent AFM force curves**

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**Figure S1.** Cyclic voltammogram of Au (111) in BMIPF<sub>6</sub> ionic liquid.

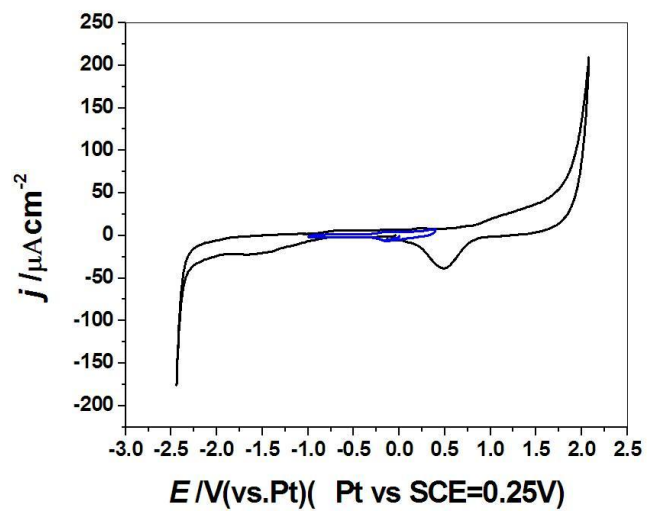
**Figure S2.** *Q-E* curve of Au (111) in BMIPF<sub>6</sub> ionic liquid for PZC measurement.

**Figure S3.** In-situ AFM image of Au (111) in BMIPF<sub>6</sub>.

**Note S1.** About Au-coated Si probes

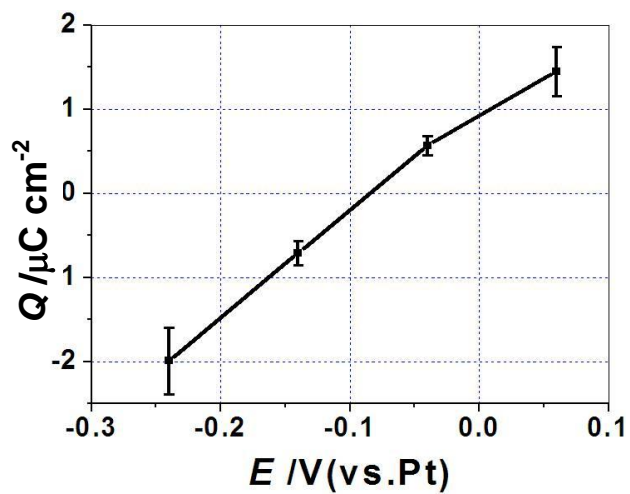
It was found that for each newly employed Au-coated AFM tip, the first several tens of force curves appeared very noisy and unstable without showing sawtooth-like transitions. Reproducible force curves could only be obtained after practicing of approaching and withdrawing procedures for as many as several tens of times. It is therefore very likely that the Au coating at the tip apex was already removed after experiencing the first several tens approaching and withdrawing. In other words, the reproducible force curves presented in this work were actually recorded with the bare Si tip, whose surface may be only slightly charged if any. This is supported by the absence of dips on force curves at either side of potential across the PZC, which would otherwise appear because of jump-to-contact of a charged probe towards the surface at close enough distance. Therefore, despite that the Si probes were Au-coated their apexes were bare in actual use.

**Figure S1**



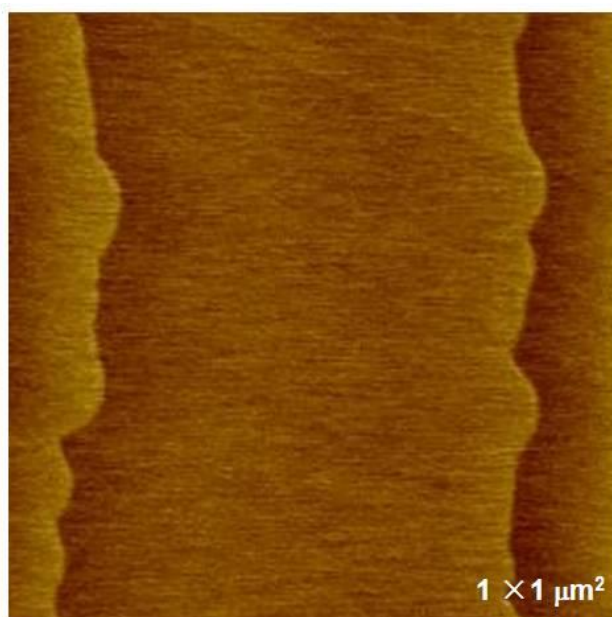
**Figure S1.** Cyclic voltammogram of Au (111) in BMIPF<sub>6</sub> ionic liquid. The AFM measurements of this work were conducted within the potential region associated with the blue line CV. Sweep rate: 50 mV s<sup>-1</sup>

Figure S2



**Figure S2.**  $Q$ - $E$  curve of Au (111) in BMIPF<sub>6</sub> ionic liquid for measurement of potential of total zero charge (PTZC) using emersion method. Refer to M. Gnahn, T. Pajkossy, D. M. Kolb *Electrochimica Acta*, 2010, **55** 6212. By fitting the experimental data, the PTZC of the system is determined to be -0.08 V (or 0.17 V vs. SEC) . Since no immobilized species have been observed with AFM inspections at the potential region of interest, the PTZC may be regarded as the PZC of system.

**Figure S3**



**Figure S3.** In-situ AFM image of Au (111) in BMIFP<sub>6</sub> measured at open circuit potential before force experiment. Scan size:  $1 \times 1 \mu\text{m}^2$ .