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Microstructural probing of phosphonium-based ionic liquids on gold electrode using colloid probe AFM

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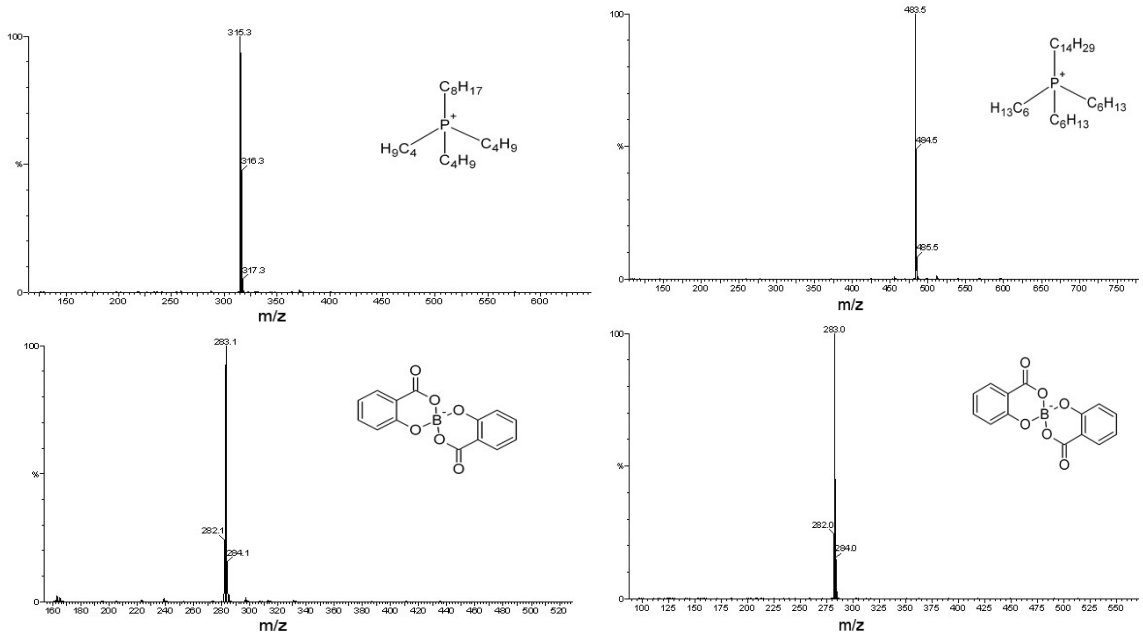


MS of $[P_{4,4,4,8}][BScB]$ MS of $[P_{6,6,6,14}][BScB]$

Figure S1. Mass spectroscopy (MS) of the synthesized $[P_{4,4,4,8}][BScB]$ and $[P_{6,6,6,14}][BScB]$ ILs.

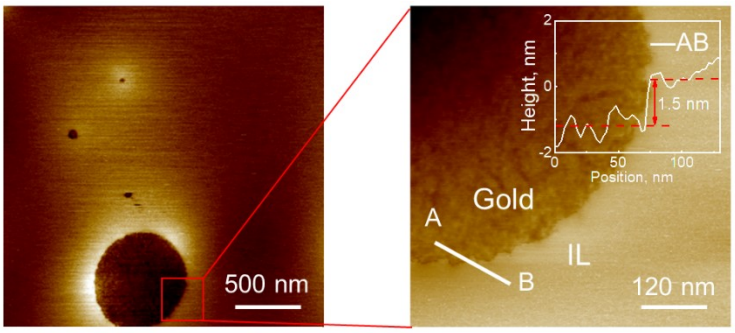
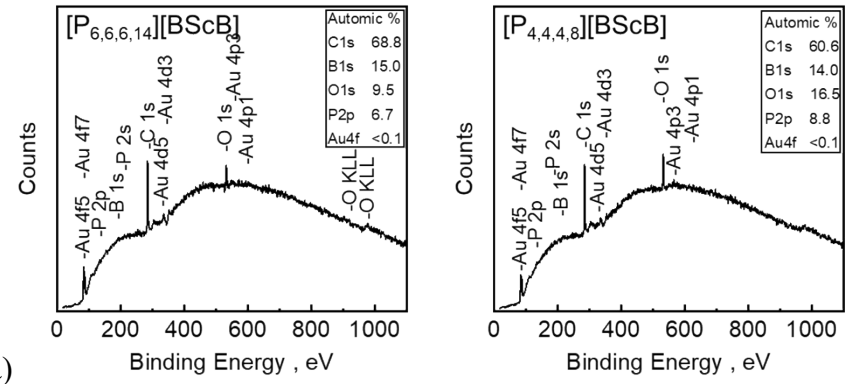
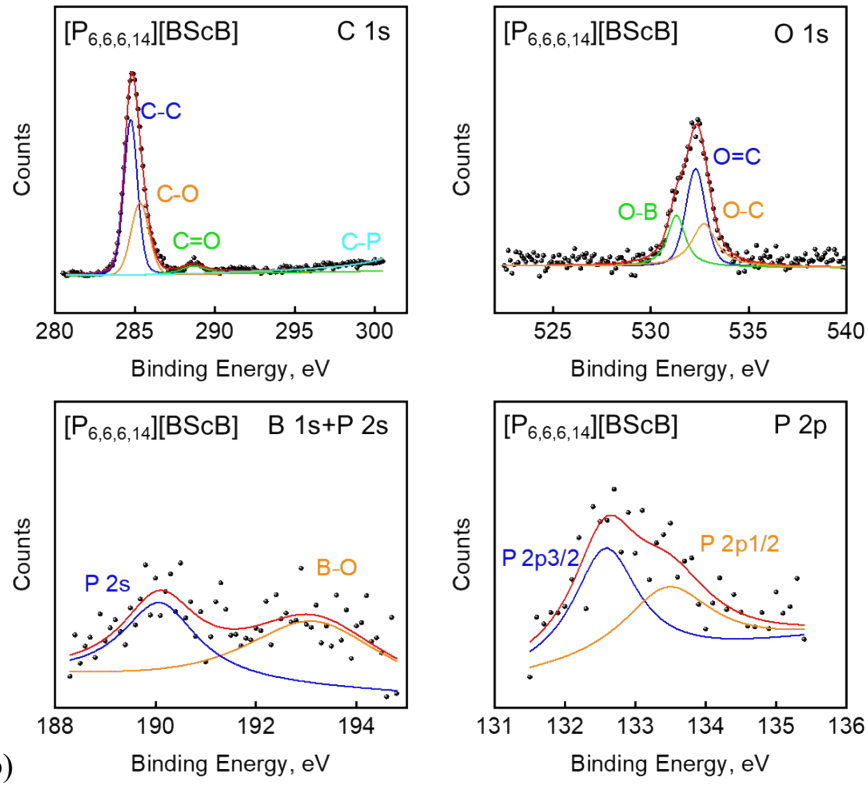


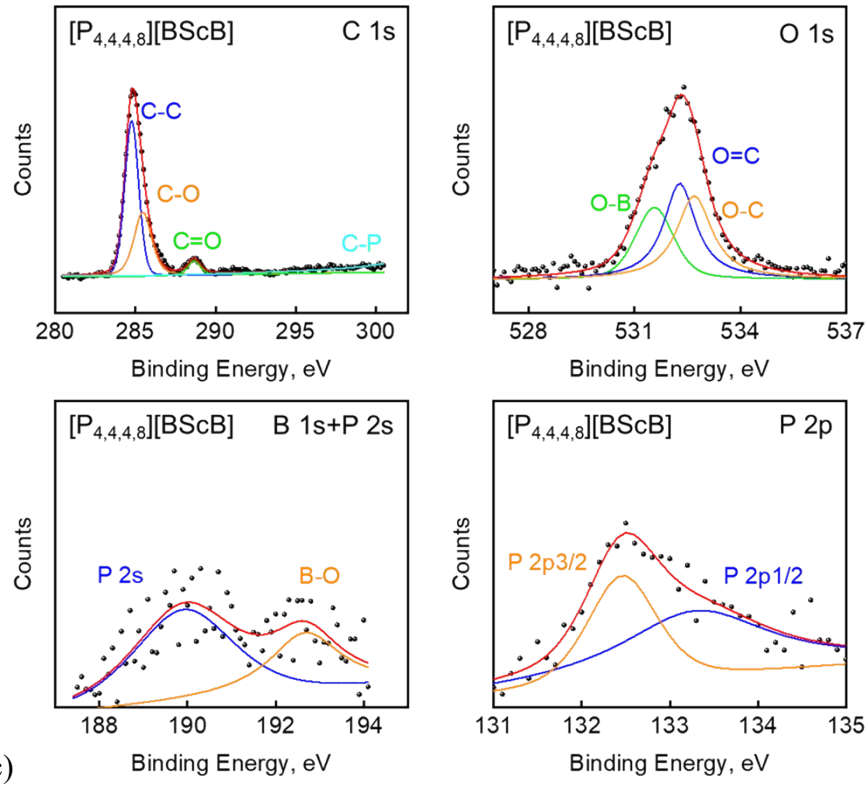
Figure S2. AFM topographic images of $[P_{6,6,6,14}][BScB]$ film on gold substrate, and the inset is the cross-sectional profile along line AB.


[P6,6,6,14][BScB]
Automic %
C1s 68.8
B1s 15.0
O1s 9.5
P2p 6.7
Au4f <0.1
-Au 4f7
-Au 4f5
-P 2p
-B 1s
-P 2s
-C 1s
-Au 4d5
-Au 4d3
-O 1s
-Au 4p3
-Au 4p1
-O KLL
-O KLL
Counts
Binding Energy , eV
[P4,4,4,8][BScB]
Automic %
C1s 60.6
B1s 14.0
O1s 16.5
P2p 8.8
Au4f <0.1
-Au 4f7
-Au 4f5
-P 2p
-B 1s
-P 2s
-C 1s
-Au 4d5
-Au 4d3
-O 1s
-Au 4p3
-Au 4p1
Counts
Binding Energy , eV

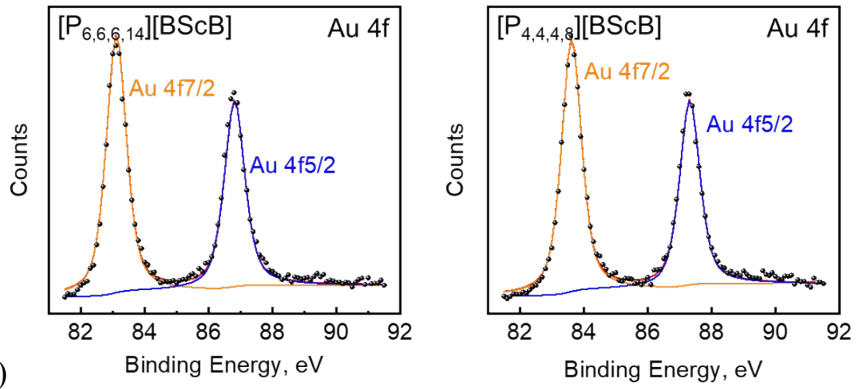
(a)


[P6,6,6,14][BScB] C 1s
C-C
C-O
C=O
C-P
Counts
Binding Energy, eV
[P6,6,6,14][BScB] O 1s
O=C
O-B
O-C
Counts
Binding Energy, eV
[P6,6,6,14][BScB] B 1s+P 2s
P 2s
B-O
Counts
Binding Energy, eV
[P6,6,6,14][BScB] P 2p
P 2p3/2
P 2p1/2
Counts
Binding Energy, eV

(b)



(c)



(d)

Figure S3. (a) XPS full spectra and C 1s, O 1s, B 1s + P 2s, and P 2p spectra of (b) $[P_{6,6,6,14}][BScB]$ and (c) $[P_{4,4,4,8}][BScB]$ on gold. (d) Au 4f spectra of $[P_{6,6,6,14}][BScB]$ and $[P_{4,4,4,8}][BScB]$ on gold.

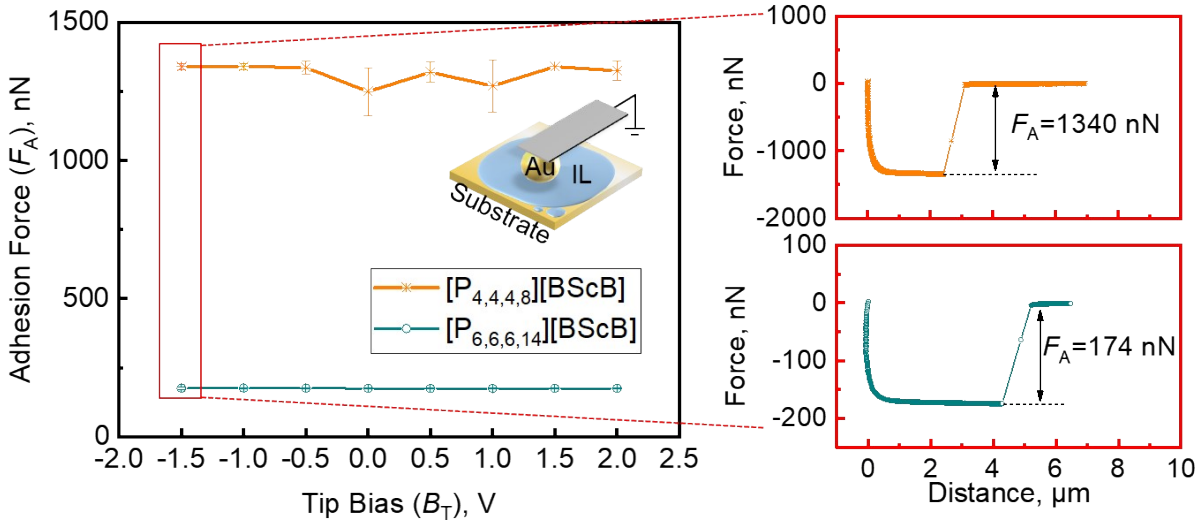


Figure S4. Left: Adhesion forces of gold colloid probe interacting with the ILs ($[P_{6,6,6,14}][BScB]$, $[P_{4,4,4,8}][BScB]$) supported by gold surfaces with varying biased voltages applied on the probe (B_T, ranging from -1.5 V to +2 V). Error bars are the standard deviation of the three measurements, which are too small to be visible in the case of $[P_{6,6,6,14}][BScB]$. Right: Representative retracting force-distance curves for $[P_{6,6,6,14}][BScB]$ and $[P_{4,4,4,8}][BScB]$ under a biased voltage of -1.5 V.

The adhesion forces of the gold colloid probe interacting with the IL films are measured under varying applied biased voltages (B_T, ranging from -1.5 V to +2 V), as shown in Figure S4. The adhesion forces remain approximately constant for both $[P_{6,6,6,14}][BScB]$ and $[P_{4,4,4,8}][BScB]$ as the biased voltages vary from -1.5 V to +2 V. This indicates the applied biased voltages have no significant influence on the adhesion forces of the ILs. However, the $[P_{6,6,6,14}][BScB]$ reveals a much smaller magnitude of the adhesion forces (~170 nN) as compared with the $[P_{4,4,4,8}][BScB]$ (~1300 nN). This might be due to the better wettability of the gold surface by $[P_{6,6,6,14}][BScB]$ which is facilitated by the longer alkyl chains of the $[P_{6,6,6,14}]^+$ cation.

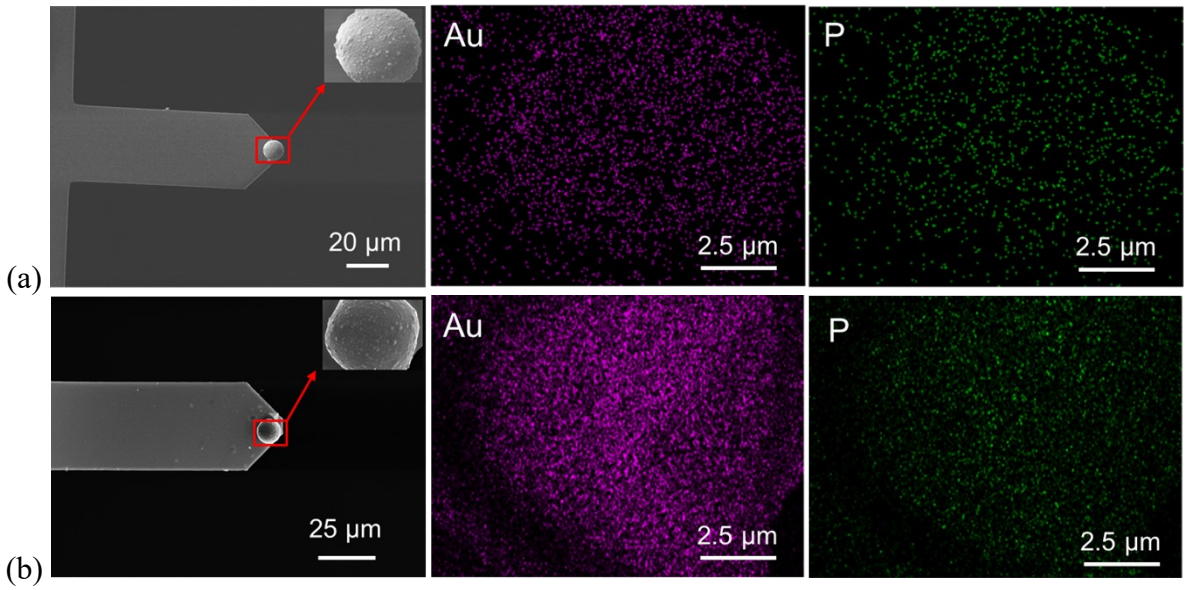


Figure S5. Typical SEM images and EDS elemental maps (Au and P elements) of the gold colloid probes after adhesion measurements on the films of (a) $[P_{6,6,6,14}][BScB]$ and (b) $[P_{4,4,4,8}][BScB]$. Insets are magnified SEM images of the gold colloid probes.

To examine whether the measured adhesion forces originating from IL-gold interfaces or the ILs films, the gold colloid probes are further analyzed by SEM coupled with energy dispersive X-ray spectroscopy (EDS) after adhesion measurements. Typical SEM images and EDS elemental maps (Au and P elements) of gold colloid probes on $[P_{6,6,6,14}][BScB]$ and $[P_{4,4,4,8}][BScB]$ after adhesion measurements are shown in Figure S5. The EDS elemental mapping results of Au and P elements on the colloid gold probes reveal that the P elements from the ILs are homogenously distributed over the surface of the gold probe, no matter which IL the probe contacted during the adhesion measurements. This provides an evidence that the measured adhesion forces originate from the ILs films, since they are attached to the surface of the gold probe after the measurements. Thus, the IL-IL interaction force of the $[P_{6,6,6,14}][BScB]$ is weaker than the $[P_{4,4,4,8}][BScB]$.