

Lubrication Mechanism of Phosphonium Phosphate Ionic Liquid in Nanoscale Single-Asperity Sliding Contacts

Z. Li, J. T. Sadowski

To be published in "Advanced Materials Interfaces"

July 2020

Center for Functional Nanomaterials
Brookhaven National Laboratory

U.S. Department of Energy
USDOE Office of Science (SC), Basic Energy Sciences (BES) (SC-22)

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Lubrication Mechanism of Phosphonium Phosphate Ionic Liquid in Nanoscale Single-Asperity Sliding Contacts

*Zixuan Li, Andrei Dolocan, Oscar Morales-Collazo, Jerzy T. Sadowski, Hugo Celio, Robert Chrostowski, Joan F. Brennecke, and Filippo Mangolini**

Z. Li, Dr. A. Dolocan, Dr. H. Celio, R. Chrostowski, Dr. F. Mangolini
Texas Materials Institute, The University of Texas at Austin, Austin, TX 78712, USA

*E-mail: filippo.mangolini@austin.utexas.edu

Z. Li, R. Chrostowski
Materials Science and Engineering Program, The University of Texas at Austin, Austin, TX 78712, USA

Dr. O. Morales-Collazo, Dr. J. F. Brennecke
McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712, USA

Dr. J. T. Sadowski
Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

Dr. F. Mangolini
J. Mike Walker Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX 78712, USA

Keywords: ionic liquids, lubrication, surface adsorption, single asperity, surface analysis

While phosphonium phosphate ionic liquids have been evaluated as additives for engine oils owing to their excellent physico-chemical properties, miscibility with hydrocarbon fluids, and promising tribological properties, their lubrication mechanism is still not established. Here, we perform atomic force microscopy nanotribological experiments using diamond-like carbon-coated silicon tips sliding on air-oxidized steel in neat trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate ionic liquid. The AFM results indicate a reduction in friction only after the removal of the native oxide layer from steel. Laterally-resolved analyses of the steel surface chemistry reveal a higher concentration of bis(2-ethylhexyl)phosphate ions adsorbed on regions where the native oxide was mechanically removed together with a change in surface electrostatic potential. These surface modifications are proposed to be induced by a

change in adsorption configuration of bis(2-ethylhexyl)phosphate anions on metallic iron compared to their configuration on iron oxide together with a reduction of surface roughness, which lead to the formation of a densely-packed, lubricious boundary layer only on metallic iron.

1. Introduction

Lubricants for mechanical systems (*e.g.*, internal combustion engines) are based on mineral or synthetic oils. To improve the properties of these fluids, additives are commonly added to the base oil. Among them, surface-active ingredients are employed to reduce friction and/or wear in the boundary-lubrication regime, where sliding speeds are too low and loads too high for a full fluid lubricating film to be maintained.^[1] These surface-active molecules achieve their lubricating function by adsorbing and/or reacting with sliding surfaces, which creates sacrificial, low-shear-strength layers (also called “tribofilms”) that prevent hard/hard contact between the sliding counterparts.^[2–5]

Among the additives that are used to reduce wear (so-called “anti-wear”), zinc dialkyldithiophosphates (ZDDPs) have been successfully employed since the 1940s.^[6,7] The most generally accepted view of ZDDP anti-wear action on steel involves the surface reaction of ZDDP to form patchy, glassy films composed of short-chain iron/zinc poly-(thio)phosphates in the bulk, with an outer layer of long-chain zinc poly-(thio)phosphates and a sulfur-rich layer near the metal surface.^[8,9] In spite of the effectiveness of ZDDPs, the large amounts of phosphorus, sulfur, and zinc in these additives, which are known to cause clogged filters and catalyst degradation in exhaust systems for automobile engines,^[10,11] have brought the environmental consequences of using ZDDPs into focus. Consequently, the permissible levels of sulfated ash, phosphorus, and sulfur (SAPS) in oil formulations have been progressively limited in modern engine-lubricant specifications.^[12]

Among the different molecules proposed as replacements or supplements to ZDDPs, ionic liquids (ILs) have captured significant interest in lubrication science in the last two decades. ILs are salts with melting temperatures below 100°C.^[13–15] They are composed of an organic cation and a weakly coordinated anion. ILs are desirable lubricant additives, since their exceptional properties (high thermal stability, negligible vapor pressure, and low flammability)^[14,16,17] together with the possibility of synthesizing air-stable ILs with a large variety of structures and functionalities,^[18,19] make them suitable for applications involving extreme conditions (*e.g.*, high temperatures, low pressures),^[20–24] such as those found in engines, space components, and micro-electromechanical systems. Since the first report in 2001 proposing the use of ILs for lubrication,^[14] a number of studies have been published on the lubrication mechanism of ILs, most of which focused on imidazolium-,^[22,25] phosphonium-,^[26,27] or phosphate-based ILs.^[28]

Studies at the nanoscale have ascribed the lubrication mechanism of ILs to their adsorption and confinement between smooth surfaces, in absence of any mechano-chemical reactions.^[4,29,30] The confined ions resist being “squeezed out” when surfaces are compressed, thus resulting in a film that prevents direct contact between the two surfaces. The properties and dynamic behavior of the adsorbed films are dependent on surface chemistry, charges and applied potentials, molecular structures of the ILs, as well as environmental conditions.^[4,31–33] While these nanotribological studies have provided significant insights into IL-mediated lubrication for tribological contacts that involve no chemical reactions between ILs and solid surfaces, studies at the macroscale, which were performed at much higher applied normal pressures and temperatures, provided evidence for the mechano-chemical reaction between IL and metallic surfaces.^[34,35] Among the ILs that have been shown to react on solid surfaces under the combined action of normal pressures and shear stresses, phosphonium phosphate ILs (PP-ILs) have been explored extensively due to their good miscibility with hydrocarbon fluids.^[36] Qu *et al.* showed that PP-ILs tribochemically react at steel/cast iron sliding

interfaces to form surface layers suggested to consist of iron phosphate. These layers were proposed to act as sacrificial films that significantly lower friction and wear rates in the case of steel/cast iron contacts.^[26,37,38] The formation of these phosphate-based tribolayers is similar to the ones found in other systems lubricated with organophosphates (e.g., tricresyl phosphate^[39]).

In spite of the relevance of these studies, a consensus about the mechanism leading to the formation of a protective layer in the case of ILs is still lacking. Additionally, no models conclusively capture the nucleation and growth of these layers formed at IL/solid interfaces. Previously published studies showing tribofilm formation were carried out at the macroscale, where the multi-asperity nature of the buried interface does not allow for accurate control of the local contact stress and geometry within the contact area or for the visualization and quantification of the events taking place between sliding counterparts. Recently, atomic force microscopy (AFM) emerged as an ideal tool for the *in situ* evaluation of mechano-chemical reactions at sample surfaces. In the case of ZDDP, Gosvami *et al.* employed AFM to visualize, for the first time, the nucleation and morphological evolution of ZDDP tribofilms during sliding.^[40] In spite of the powerfulness of AFM for fundamental studies in tribology and lubrication science, it does not provide any detailed information about the compositions or structures of the tribofilms. Chemical analysis of these films has been a challenging surface science problem due to their reduced thickness and the small areas scanned during AFM experiments.

Here, we combine *in situ* single-asperity AFM tests and *ex situ* laterally-resolved surface analyses to establish a fundamental understanding of the lubrication mechanism of a class of PP-ILs, namely trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ([P_{6,6,6,14}][DEHP]). The AFM results show a significant friction reduction only upon removing the native oxide layer from the steel surface. Subsequent spatially-resolved surface characterizations by synchrotron-based X-ray photoemission electron spectroscopy (X-

PEEM), low energy electron microscopy (LEEM), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) reveal that no mechano-chemical reaction occurred between the $[P_{6,6,6,14}][DEHP]$ IL and metallic iron. However, the surface-analytical results indicate an increase in concentration of surface-adsorbed bis(2-ethylhexyl) phosphate ions in regions scanned by the AFM tip where the native oxide was mechanically removed together with a change in surface electrostatic potential. These surface modifications are proposed to be induced by changes in surface roughness and adsorption configuration of bis(2-ethylhexyl) phosphate ions on metallic iron compared to the one on iron oxide, which results in the formation of a densely-packed, lubricious boundary layer only on metallic iron.

2. Results

2.1. *In situ* Nanotribological Experiments

AFM experiments were performed in pure $[P_{6,6,6,14}][DEHP]$ IL to evaluate *in situ*, in single-asperity sliding nanocontacts the mechano-chemical phenomena occurring at steel/IL interfaces. Specifically, the AFM tip was slid against air-oxidized 52100 steel at 111°C while immersed in pure $[P_{6,6,6,14}][DEHP]$ IL. A high normal stress (7.3 ± 0.4 GPa) was applied while scanning a $2 \times 2 \mu m^2$ area (referred to as highly-loaded area – HLA – in the following) to mimic a single asperity within a typical multi-asperity contact in the boundary lubrication regime, whereas zoomed-out images enclosing the HLA were periodically acquired at a nonperturbative load with the aim of visualizing and quantifying changes in surface morphology and friction forces (see **Figure 1**).^[40] **Figure 2** displays $5 \times 5 \mu m^2$ AFM topography images and the corresponding normalized friction force maps after scanning the central $2 \times 2 \mu m^2$ area for different numbers of sliding cycles. The AFM images indicate a progressive removal of material (*i.e.*, wear) and an increased contrast in the friction force maps with sliding cycles. To quantitatively evaluate the amount of material removed while scanning at high loads, the height difference (ΔH) between the mean plane of the HLA and the mean plane of the reference area (RA) was computed as shown in the schematic in **Figure**

3a. Similarly, the evolution of the friction forces in the HLA relative to the friction forces in the RA was evaluated by computing the difference (ΔF) between the mean values of the friction force histograms (fitted with Gaussian synthetic curves, see **Figure 3b**) obtained from these two regions. **Figure 3c** displays the evolution of ΔF as a function of ΔH , while **Figure S.1** in the Supporting Information presents the changes of ΔH and ΔF with sliding cycles. Upon removing the first ~ 4 nm of the steel surface, which is a depth from the sample surface comparable to the thickness of the native oxide layer on steel substrates (estimated to be 3.8 ± 0.4 nm on the basis of XPS data acquired on a polished and aged 52100 steel substrate^[41]), a progressive reduction in friction forces was observed in the HLA. After the removal of the first ~ 4 nm, ΔF reached a steady state value. Additionally, the topographic AFM images reveal a decrease in surface roughness in the region scanned by the AFM tips at high pressure for 1000 cycles (**Figure S.2** in the Supporting Information). Load-dependent friction measurements were performed in the HLA and RA to highlight changes in nanoscale friction due to variations in surface chemistry (**Figure S.3** in the Supporting Information). The friction forces measured in the RA are larger than the friction forces measured in the HLA for all applied loads. Additionally, the slope of the least squares fitting of the load-dependent friction data acquired in the RA is larger than the slope of the least squares fitting of the load-dependent friction data acquired in the HLA, thus substantiating the contrast appearing in the friction force maps shown in **Figure 2**.

2.2. Laterally-Resolved Surface Analyses

To identify any surface chemical changes occurring in the HLA scanned by the AFM tip in the presence of [P_{6,6,6,14}][DEHP] IL and leading to friction reduction, *ex situ* surface chemical analyses were performed. Synchrotron-based X-PEEM allows for the acquisition of both X-ray absorption near edge structure (XANES) and X-ray photoelectron spectroscopy (XPS) data with a high lateral resolution (down to 20 nm). An X-PEEM image taken at 138

eV is displayed in **Figure 4a** together with phosphorus 2p XANES (**Figure 4b**) and XPS (**Figure 4c**) spectra extracted from two regions of interests, namely the HLA and the RA. No significant differences were observed in the extracted XANES spectra (**Figure 4b**): both XANES P 2p spectra exhibit a broad envelope with pre-edge shoulders at about 135.9 eV (a) and 136.7 eV (b), which are attributed to the transition of phosphorus 2p electrons to unoccupied 3s antibonding orbitals. The main peaks at about 138.6 eV (c) and 146.3 eV (d) correspond to transitions from phosphorus 2p electrons to 3p- and 3d-like antibonding states, respectively.^[42,43] No significant differences could be observed between the spectra extracted from the HLA and the RA regions, which suggests that no change in phosphorus bonding configuration occurred in the area scanned at high loads compared to the region scanned at lower pressures. Notably, the absence of any intense, energy-resolvable pre-edge absorption features near shoulders (a) and (b) indicate that no inorganic long-chain polyphosphates are formed in the near-surface region of the sample.^[44] The occurrence of no tribochemical reaction in the HLA is corroborated by XANES Fe 2p analyses (**Figure S.4**). Since the reference XANES P 2p spectrum of [P_{6,6,6,14}][DEHP] IL exhibits a broad absorption envelope that makes it challenging to unambiguously identify the characteristic spectral contributions of [P_{6,6,6,14}] and [DEHP] ions, XPS P 2p spectra were also acquired both at the synchrotron facility and using a laboratory-based system. **Figure 4c** displays the synchrotron XPS P 2p spectra acquired at a photon energy of 380 eV. In agreement with the XANES results, no significant differences could be found between the spectra obtained from the HLA and RA. Notably, the synchrotron XPS spectra are comparable to P 2p XPS spectra acquired using a laboratory-based XPS instrument on a reference sample left in contact with [P_{6,6,6,14}][DEHP] IL at the same temperature of the AFM nanotribological tests (*i.e.*, 111°C) and for the same period of time as the duration of the AFM tests, but without being scanned by AFM tips (lab-based XPS data shown in **Figure S.5**). In other words, the steel surface was treated similarly to the RA of the samples used in AFM experiments. The higher signal-to-noise spectra allow

for unambiguous fits of the spectra with synthetic curves, which indicate the adsorption of both [DEHP] anions and $[P_{6,6,6,14}]$ cations on the air-oxidized steel surface with a slight enrichment of [DEHP] anions. The XPS results also suggest that no thermo-chemical reactions leading to the formation of inorganic (poly)phosphates occurred between $[P_{6,6,6,14}][\text{DEHP}]$ IL and steel (see **Figure S.4** and **Table S.1**), in agreement with XANES P 2p data.

To gain further insights into the chemistry and spatial distribution of $[P_{6,6,6,14}][\text{DEHP}]$ IL ions adsorbed on steel, ToF-SIMS measurements were also performed. **Figure 5a** displays ToF-SIMS high lateral resolution (~ 200 nm) maps of several species of interest, including PO_2^- and PO_3^- (characteristic fragments of [DEHP] anions), C_2P^- (characteristic fragments of $[P_{6,6,6,14}]$ cations), and FeO_2^- , Fe^+ (from the steel substrate). The maps corresponding to the PO_3^- and PO_2^- fragments indicate a pronounced enrichment of the [DEHP] anions adsorbed in the HLA. The same enrichment could be detected for fragments of $\text{C}_4\text{H}_2\text{POFe}_2^-$, which indicates both the chemisorption of phosphate anions through the formation of P-O-Fe linkages and the presence of alkyl chains attached to the phosphate head group. In contrast, the ToF-SIMS map for the C_2P^- fragment, corresponding to the $[P_{6,6,6,14}]$ cations, does not show any significant intensity contrast between the HLA and RA. The distributions of two characteristic fragments for the steel substrate, namely FeO_2^- and Fe^+ (the latter was acquired from a separate sample in positive polarity), were also analyzed: while in the case of FeO_2^- map a decrease in intensity was observed in the HLA with a slight increase near the boundary, which indicates mechanical removal of iron oxide through the mechanical action of the scanning AFM tip, the map for the Fe^+ fragment shows a slight increase in intensity in the region scanned at higher load.

To obtain information about the in-depth chemical distribution of molecular fragments in the near-surface region of steel, ToF-SIMS depth profiling was employed on a $100 \times 100 \mu\text{m}^2$ area using the same reference sample analyzed by lab-based XPS (*i.e.*, an air-oxidized

steel substrate sample left in contact with $[P_{6,6,6,14}][DEHP]$ IL at 111°C for the same period of time of the duration of the AFM tests, but without being scanned by AFM tips). Based on the evolution of the intensity of several fragments with sputtering time, an adsorbed molecular layer was identified (shown in **Figure 5b** by tracking the C_7^- fragments), followed by a metallic layer of the steel substrate (shown in **Figure 5b** by tracking the Fe_4^- fragments). Within the molecular layer, we also found characteristic fragments from both the [DEHP] anions ($C_{12}H_2PO_2^-$, $C_4H_2POFe_2^-$, and $CHPO_4Fe_2^-$) and the $[P_{6,6,6,14}]$ cations (C_5P^+). Altogether, the ToF-SIMS results indicate that while both $[P_{6,6,6,14}]$ cations and [DEHP] anions are adsorbed on oxidized steel, but a much higher concentration of the latter was adsorbed in the HLA (where the native oxide had been mechanically removed in the former) than the RA. Additionally, the detection of fragments corresponding to alkylated iron phosphates suggests that no mechano-chemical reaction occurred between $[P_{6,6,6,14}][DEHP]$ and steel during AFM nanotribological testing to form an inorganic phosphate layer, in agreement with the XPS results.

To evaluate the effect of the higher concentration of adsorbed ions in the HLA on the electronic structure of the surface, LEEM measurements were performed. LEEM is ideally suited for displaying lateral variations in surface electrostatic potential, as the high-energy electrons are decelerated to energies close to zero by the negative voltage applied to the sample and become surface sensitive. By tuning the potential applied to the specimen, a transition from mirror-mode (where all electrons are reflected and do not reach the surface) to LEEM-mode (where the electrons reach the sample and are subsequently backscattered) occurs. The transition is accompanied by the appearance of an inflection point in the electron intensity versus electron energy curves (usually referred to as I-V measurements). Changes in surface potential of materials have been shown to lead to shifts in the inflection point in I-V curves.^[45,46] **Figure 6** displays a LEEM image acquired at an electron energy of 2.3 eV together with I-V curves extracted from the HLA and the surrounding region. The I-V curves

exhibit similar shapes, but the one extracted from the HLA is shifted to lower energy compared to the one from the RA, indicating a change in surface electrostatic potential in the HLA due to changes in number density of surface-adsorbed ions as well as their spatial orientation. Similar changes in surface potentials of metals have been observed upon forming self-assembled monolayers (SAMs) and ascribed to the presence of highly ordered arrays of molecular surface dipoles oriented on the surface.^[47,48]

3. Discussion

Based on the AFM results and the outcomes of the surface-analytical investigation of steel surfaces after the nanotribological testing, the following model is proposed for explaining the lubrication mechanism of [P_{6,6,6,14}][DEHP] IL on steel (**Figure 7**). Upon exposing air-oxidized steel surfaces to [P_{6,6,6,14}][DEHP] IL at 111°C, surface adsorption of anions and cations of [P_{6,6,6,14}][DEHP] IL occurs, as suggested by X-PEEM and ToF-SIMS data. As the AFM tip scans the air-oxidized steel surface at high loads, the IL ions are compressed at the tip leading edge and compose a densely-packed adsorbed layer that aids in friction reduction, as commonly seen in the case of AFM tips sliding on SAMs.^[2] The high-pressure applied by the AFM tip, however, does not inhibit the removal of the native iron oxide layer (demonstrated by AFM topography images and ToF-SIMS maps of FeO₂⁻ and Fe⁺), which leads to the exposure of metallic iron to the [P_{6,6,6,14}][DEHP] IL. Density functional theory (DFT) analysis by Huong *et al.* indicates that phosphate ions have a stronger interaction energy (*i.e.*, higher enthalpy of adsorption) on iron than on iron oxide. Additionally, phosphates bind to metallic iron surfaces through multipoint interactions of oxygen atoms with iron atoms, while on iron oxide surfaces a monodentate configuration is energetically favorable for adsorbed phosphates.^[49] Thus, the mechanical stress applied by the AFM tip not only compresses the ions to a higher packing density especially at the tip leading edge, but also removes the native oxide layer from the steel surface and exposes metallic iron

to the $[P_{6,6,6,14}][DEHP]$ IL, which leads to a change in the geometric configuration of surface-bound alkylated phosphate groups from monodentate (on iron oxide) to bidentate (on metallic iron). The mechanically-induced removal of the native oxide from the steel also results in a decrease in surface roughness in the area scanned at high loads. As shown by Ewers and Batteas for the case of alkylsilane SAMs on nanoparticles,^[50] the nanoscopic curvature of solid surfaces strongly influences the configuration and lubricity of SAMs: the packing density of SAMs is relatively low on curved surfaces, thus leading to a high free volume and low structural rigidity, both of which negatively affect their ability to reduce friction. In light of this, the lateral confinement induced by the AFM tip together with the reduced roughness in the region scanned at higher loads is proposed to increase the interaction between the alkyl chains of surface-adsorbed $[DEHP]$ ions. This, together with a corresponding orientation of molecular dipoles normal to the surface, results in changes in surface potential as indicated by LEEM measurements. The formation of this densely-packed, highly-ordered boundary layer on metallic iron aids in friction reduction at low loads (as those used for the periodic acquisition of friction images, **Figure 2**), in a similar manner to the molecular mechanism of boundary lubrication of self-assembled or Langmuir-Blodgett monolayers.^[51–53] While this boundary layer effectively reduces friction in nanoscale DLC/steel contacts, it does not prevent wearing the steel surface at high loads (such as the one applied by the AFM tip in the HLA, *i.e.*, 7.3 ± 0.4 GPa), as suggested by the progressive removal of material from the steel substrate (**Figure S.1a**).

Finally, it is critical to highlight that the present study was carried out under completely different contact conditions compared to previous reports published in the literature,^[26,54–56] which provided evidence for the tribochemical reaction between $[P_{6,6,6,14}][DEHP]$ and steel or cast iron surfaces and the formation of inorganic phosphate tribofilms. Due to the reduced sliding speed employed in this work, a negligible temperature rise ($< 1^\circ\text{C}$) occurred at the contact (see calculations in the Supporting Information). This is

in contrast to macroscale studies, in which the elevated sliding speeds combined with the multi-asperity nature of sliding contacts could lead to a large increase in contact temperature (as high as 140°C), thus significantly increasing the rate of any tribolochemical reaction.

4. Conclusion

We performed *in situ* AFM single-asperity nanotribological experiments to visualize and quantify the stress-assisted processes occurring at the interface between air-oxidized steel and [P_{6,6,6,14}][DEHP] IL. The AFM results indicate a significant reduction in friction only after the removal of the native surface oxide layer on the steel. Subsequent *ex situ* laterally-resolved analysis of the surface chemistry of steel by X-PEEM indicates that no stress-assisted, thermally-activated chemical reaction occurred between the [P_{6,6,6,14}][DEHP] IL and steel during the AFM experiments. The removal of the native oxide from steel led to significant variations in surface potential (measured by LEEM) and an increase in surface coverage of [DEHP] ions (measured by ToF-SIMS). These surface modifications are proposed to be caused by a change in surface roughness, and adsorption configuration of bis(2-ethylhexyl)phosphate anions on metallic iron compared to their configuration on iron oxide, which lead to the formation of a densely-packed, lubricious boundary layer only on metallic iron. These findings not only shed new light on the lubrication mechanism of ILs in general, but also provide guidance for engineering ILs with the aim of tuning their lubricating properties by controlling their interfacial structures with metal and metal oxides.

5. Experimental Section

Synthesis of [P_{6,6,6,14}][DEHP] IL. In a round bottom flask (500 mL) a solution of trihexyl(tetradecyl)phosphonium bromide ([P_{6,6,6,14}][Br], 95% purity, Strem Chemicals) (10.0 g, 17.7 mmol) in methanol (200 mL, 99.8% purity, J.T Baker) was treated with Amberlite IRN78 (53 g, 99.9%, purity, Alfa Aesar) and mixed until no residual halide precipitation was observed by AgNO₃ test to obtain trihexyl(tetradecyl)phosphonium hydroxide

([P_{6,6,6,14}][OH]). The mixture was filtered and treated with bis(2-ethylhexyl) hydrogen phosphate (5.72 g, 17.7 mmol, TCI) and stirred for 2 days. Methanol and other volatiles were removed at 323.15 K under reduced pressure (7.5 Torr). Complete removal of volatiles was confirmed by ¹H NMR. Water byproduct was then removed by further drying at 323.15 K under reduced pressure for approximately 3 days. The water content of the synthesized IL was determined by a Brinkman 831 Karl Fischer coulometer and was less than 0.05% by weight (or 500 ppm). The structures of the ILs were verified by ¹H NMR (Varian INOVA-600) spectroscopy with dried ILs dissolved in deuterated dimethyl sulfoxide (DMSO-*d*₆, 99.9 atom %D, Sigma-Aldrich) containing 1% v/v TMS. The purity of as-synthesized [P_{6,6,6,14}][DEHP] IL was estimated to be ≥90% by NMR spectroscopy. Any residual halide in the aqueous phase in contact with the ILs was not detectable by adding an AgNO₃ aqueous solution.

AFM Experiments. AFM experiments were performed using an MFP-3D Origin+ AFM (Oxford Instruments Asylum Research, Santa Barbara, CA, USA), equipped with a liquid cell with temperature control. The specimens used in AFM tests were made of ASTM 52100 bearing steel (McMaster-Carr, USA). Before the experiments, the substrates were mechanically polished (RMS roughness measured over a 5 x 5 μm² region: 2.1 ± 0.4 nm), sonicated in isopropanol and acetone, and stored for three days in a desiccator to allow the native oxide to grow. To carry out AFM experiments in [P_{6,6,6,14}][DEHP] IL, 52100 steel samples were coated with 0.1 g of [P_{6,6,6,14}][DEHP] IL so that the cantilever was fully immersed in the IL once engaged. The temperature of the IL-steel interface was set at 111°C with ± 1°C fluctuation. DLC-coated silicon tips (Mikromasch NSC14-Al-BS) were used to mimic single-asperity sliding contacts. The tip shape was determined before and after each experiment using the blind tip reconstruction method^[57] with ultra-nanocrystalline diamond (UNCD, Aqua 25, Advanced Diamond Technologies, USA) as the testing substrate. For the

experiments presented here, the tip shape was verified to be approximatively a single paraboloid, with small changes in shape or size after the experiments. This was accounted for when estimating the uncertainty in contact pressure. The normal spring constant and lateral spring constant of the cantilever were measured to be ~ 4.5 N/m and ~ 345.8 nN/V, via calibrations of Sader's method^[58], and the wedge method^[59], respectively. For the *in situ* evaluation of the nanotribological behavior of [P_{6,6,6,14}][DEHP] IL, a $2 \times 2 \mu\text{m}^2$ area was constantly scanned with an applied load that corresponds to an average contact pressure of 7.3 ± 0.4 GPa as computed from Hertz contact mechanics (specific parameters and equations in the Supporting Information). The sliding speed of the AFM tip was $78 \mu\text{m/s}$. To visualize the changes in surface topography and nanotribological response, zoomed-out $5 \times 5 \mu\text{m}^2$ images were periodically acquired at a non-perturbative load. To facilitate the ToF-SIMS analysis of the surface chemistry of the area scanned at high loads, new sets of samples were prepared by increasing the dimension of the HLA to $5 \times 5 \mu\text{m}^2$ (while maintaining the same pressure and sliding speed) and the size of the frame scanned at a non-perturbative scan to $10 \times 10 \mu\text{m}^2$.

X-PEEM and LEEM Surface Characterization. X-PEEM and LEEM measurements were performed at the XPEEM/LEEM endstation located at Electron Spectro-Microscopy (ESM-21-ID) beamline of the NSLS-II at Brookhaven National Laboratory (BNL, Upton, NY, USA). All measurements were conducted at a base pressure of $< 3 \times 10^{-10}$ Torr and room temperature. The aberration-corrected LEEM/PEEM system (AC-LEEM/PEEM) applied a bias of -20 kV to the steel sample. The incident X-ray beam was linearly polarized during the XANES measurements. The acquisition of spatially-resolved XANES phosphorus 2p (P 2p) spectra was performed with the photon energy between 128 eV and 158 eV and a step size of 0.1 eV. XANES spectra were processed using the Demeter software package.^[60] A pre-edge baseline subtraction and post-edge normalization were performed on the spectra. This normalization procedure makes any variations in spectral intensity arise from changes in

chemical environment. The XPS spectra were acquired using a circular selected-area aperture with a diameter of 1.5 μm and the photon energy was 380 eV.

In the case of LEEM experiments, an acceleration voltage of 20 kV was used to obtain high-energy electrons. I-V measurements were performed by scanning the potential applied to the specimen so that the effective kinetic energy of the electrons at the surface varied from 0 to 6 eV with an increment of 0.1 eV. The intensity of the back-scattered electrons was normalized to their maximum intensity.

ToF-SIMS Analysis. ToF-SIMS data was acquired using a TOF.SIMS 5 instrument (ION-TOF GmbH, Germany, 2010) equipped with a pulsed (20 ns), bismuth analysis ion gun (30 keV) and a Cs^+/O_2^+ dual sputtering ion gun (0.5/1 keV, ~ 40 nA measured sample currents). For depth profiling, the analysis gun was set in either the high current (HC, ~ 3 pA measured sample current) or burst alignment (BA, ~ 0.03 pA measured sample current, with 7 bursts) mode for high sensitivity or high lateral resolution (~ 200 nm), respectively. ToF-SIMS depth profile measurements were carried out on steel samples left in contact with 0.1 g $[\text{P}_{6,6,6,14}][\text{DEHP}]$ at 111°C for the same duration of a typical AFM nanotribological experiment, but without being scanned by an AFM tip (note: the same samples were also prepared for lab-based XPS analysis, see Supporting Information). During depth profiling in HC mode, the analysis ion beam was raster scanned over $100 \times 100 \mu\text{m}^2$ areas, using a polyatomic (Bi_3^+) source to enhance the yield of large secondary ion fragments,^[61] while in the BA mode the analysis ion beam, using a Bi_1^+ source, was raster scanned over $20 \times 20 \mu\text{m}^2$ areas. All profiles were acquired in non-interlaced mode, *i.e.*, sequential analysis and sputtering, with the sputtering ion beam raster scanning areas of $300 \times 300 \mu\text{m}^2$ centered over the analyzed areas. Given the electronegative nature of organic and oxidized fragments, we used Cs^+ sputtering to record the depth profiles in negative polarity. Similarly, as the

transition metals are electropositive, we had to use O_2^+ sputtering to acquire the depth profiles in positive polarity. All detected ions had a mass resolution ~ 6000 ($m/\delta m$) in both HC and BA modes. The molecular fragments discussed in this study were identified considering any potential secondary ion fragment originating from $[\text{P}_{6,6,6,14}][\text{DEHP}]$ IL, steel or a combination of them. All ToF-SIMS experiments were performed in ultra-high vacuum conditions ($\sim 1.5 \times 10^{-9}$ Torr).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The material is based upon work supported by the Welch Foundation (Grant No. F-2002-20190330). F.M. acknowledges support from the 2018 Ralph E. Powe Junior Faculty Enhancement Award sponsored by the Oak Ridge Associated Universities (ORAU) and from The University of Texas at Austin (UTA)/Texas Materials Institute (TMI). The NSF grant DMR-0923096 is acknowledged in conjunction to the ToF-SIMS instrument at TMI, UTA. This research used resources of the Center for Functional Nanomaterials and National Synchrotron Light Source II, which are U.S. DOE Office of Science Facilities, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] G. W. Stachowiak, A. W. Batchelor, *Engineering Tribology*, 4th ed., Butterworth-Heinemann, Waltham, MA USA **2014**.
- [2] C. M. Mate, R. W. Carpick, *Tribology on the Small Scale*, 2nd ed., Oxford University Press, Oxford, UK 2012.
- [3] M. I. de Barros'Bouchet, J. M. Martin, T. Le-Mogne, B. Vacher, *Tribol. Int.* **2005**, *38*, 257.
- [4] P. K. Cooper, J. Staddon, S. Zhang, Z. M. Aman, R. Atkin, H. Li, *Front. Chem.* **2019**, *7*, 1.
- [5] K. D. Koshigan, F. Mangolini, J. B. Mcclimon, B. Vacher, S. Bec, R. W. Carpick, J. Fontaine, *Carbon* **2015**, *93*, 851.
- [6] A. M. Barnes, K. D. Bartle, V. R. A. Thibon, *Tribol. Int.* **2001**, *34*, 389.
- [7] H. Spikes, *Tribol. Lett.* **2004**, *17*, 469.
- [8] I. Nedelcu, E. Piras, A. Rossi, H. R. Pasaribu, *Surf. Interface Anal.* **2012**, *44*, 1219.
- [9] C. Minfray, J. M. Martin, M. I. De Barros, T. Le Mogne, R. Kersting, B. Hagenhoff, *Tribol. Lett.* **2004**, *17*, 351.
- [10] D. Summers-Smith, *Tribol. Int.* **1978**, *11*, 318.
- [11] M. Z. Huq, X. Chen, P. B. Aswath, R. L. Elsenbaumer, *Tribol. Lett.* **2005**, *19*, 127.
- [12] H. Spikes, *Lubr. Sci.* **2009**, *20*, 123.
- [13] R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792.
- [14] C. Ye, W. Liu, Y. Chen, L. Yu, N. Si, *Chem. Commun.* **2001**, 2244.
- [15] K. . Marsh, J. . Boxall, R. Lichtenthaler, *Fluid Phase Equilib.* **2004**, *219*, 93.
- [16] Y. Zhou, J. Qu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 3209.
- [17] A. Somers, P. Howlett, D. MacFarlane, M. Forsyth, *Lubricants* **2013**, *1*, 3.
- [18] A. E. Somers, B. Khemchandani, P. C. Howlett, J. Sun, D. R. MacFarlane, M. Forsyth, *ACS Appl. Mater. Interfaces* **2013**, *5*, 11544.

- [19] H. Li, M. W. Rutland, R. Atkin, *Phys. Chem. Chem. Phys.* **2013**, 15, 14616.
- [20] M. Yao, M. Fan, Y. Liang, F. Zhou, Y. Xia, *Wear* **2010**, 268, 67.
- [21] A.-E. E. Jiménez, M.-D. D. Bermúdez, *Tribol. Lett.* **2007**, 26, 53.
- [22] A. Suzuki, Y. Shinka, M. Masuko, *Tribol. Lett.* **2007**, 27, 307.
- [23] K. W. Street, W. Morales, V. R. Koch, D. J. Valco, R. M. Richard, N. Hanks, *Tribol. Trans.* **2011**, 54, 911.
- [24] W. Zhao, Y. Wang, L. Wang, M. Bai, Q. Xue, *Colloids Surfaces A Physicochem. Eng. Asp.* **2010**, 361, 118.
- [25] P. M. Amorim, A. M. Ferraria, R. Colaço, L. C. Branco, B. Saramago, *Beilstein J. Nanotechnol.* **2017**, 8, 1961.
- [26] Y. Zhou, J. Dyck, T. W. Graham, H. Luo, D. N. Leonard, J. Qu, *Langmuir* **2014**, 30, 13301.
- [27] A. Hernández Battez, M. Bartolomé, D. Blanco, J. L. Viesca, A. Fernández-González, R. González, *Tribol. Int.* **2016**, 95, 118.
- [28] W. C. Barnhill, H. Luo, H. M. Meyer, C. Ma, M. Chi, B. L. Papke, J. Qu, *Tribol. Lett.* **2016**, 63, 22.
- [29] M. Han, R. M. Espinosa-marzal, *Lubricants* **2018**, 6, 64.
- [30] R. M. Espinosa-Marzal, A. Arcifa, A. Rossi, N. D. Spencer, *J. Phys. Chem. C* **2014**, 118, 6491.
- [31] J. Sweeney, F. Hausen, R. Hayes, G. B. Webber, F. Endres, M. W. Rutland, R. Bennewitz, R. Atkin, *Phys. Rev. Lett.* **2012**, 109, 155502.
- [32] R. M. Espinosa-Marzal, A. Arcifa, A. Rossi, N. D. Spencer, *J. Phys. Chem. Lett.* **2014**, 5, 179.
- [33] B. Yu, F. Zhou, Z. Mu, Y. Liang, W. Liu, *Tribol. Int.* **2006**, 39, 879.
- [34] Y. Zhou, D. N. Leonard, W. Guo, J. Qu, *Sci Rep* **2017**, 7, 8426.
- [35] V. Sharma, C. Gabler, N. Doerr, P. B. Aswath, *Tribol. Int.* **2015**, 92, 353.

- [36] B. Yu, D. G. Bansal, J. Qu, X. Sun, H. Luo, S. Dai, P. J. Blau, B. G. Bunting, G. Mordukhovich, D. J. Smolenski, *Wear* **2012**, 289, 58.
- [37] J. Qu, D. G. Bansal, B. Yu, J. Y. Howe, H. Luo, S. Dai, H. Li, P. J. Blau, B. G. Bunting, G. Mordukhovich, D. J. Smolenski, *ACS Appl. Mater. Interfaces* **2012**, 4, 997.
- [38] J. Qu, H. Luo, M. Chi, C. Ma, P. J. Blau, S. Dai, M. B. Viola, *Tribol. Int.* **2014**, 71, 88.
- [39] R. Lu, K. Kobayashi, H. Nanao, S. Mori, *Tribol. Lett.* **2009**, 33, 1.
- [40] N. N. Gosvami, J. A. Bares, F. Mangolini, A. R. Konicek, D. G. Yablon, R. W. Carpick, *Science* **2015**, 348, 102.
- [41] F. Mangolini, *Ph.D. Thesis*, ETC Zurich, **2011**.
- [42] V. Sharma, N. Doerr, P. B. Aswath, *RSC Adv.* **2016**, 6, 22341.
- [43] J. Kruse, W. Negassa, N. Appathurai, L. Zuin, P. Leinweber, *J. Environ. Qual.* **2010**, 39, 2179.
- [44] M. Nicholls, M. N. Najman, Z. Zhang, M. Kasrai, P. R. Norton, P. U. P. A. Gilbert, *Can. J. Chem.* **2007**, 85, 816
- [45] N. Barrett, J. E. Rault, J. L. Wang, C. Mathieu, A. Locatelli, T. O. Menten, M. A. Niño, S. Fusil, M. Bibes, A. Barthélémy, D. Sando, W. Ren, S. Prosandeev, L. Bellaiche, B. Vilquin, A. Petraru, I. P. Krug, C. M. Schneider, *J. Appl. Phys.* **2013**, 113.
- [46] L. Aballe, S. Matencio, M. Foerster, E. Barrena, F. Sánchez, J. Fontcuberta, C. Ocal, *Chem. Mater.* **2015**, 27, 6198.
- [47] S. D. Evans, A. Ulman, *Chem. Phys. Lett.* **1990**, 170, 462.
- [48] B. De Boer, A. Hadipour, M. M. Mandoc, T. Van Woudenberg, P. W. M. Blom, *Adv. Mater.* **2005**, 17, 621.
- [49] H. T. T. Ta, A. K. Tieu, H. Zhu, H. Yu, T. D. Ta, S. Wan, N. V. Tran, H. M. Le, *J. Phys. Chem. C* **2018**, 122, 635.
- [50] R. L. Jones, N. C. Pearsall, J. D. Batteas, *J. Phys. Chem. C* **2009**, 113, 4507.
- [51] Q. Zhang, L. A. Archer, *J. Phys. Chem. B* **2003**, 107, 13123.

- [52] V. DePalma, N. Tillman, *Langmuir* **1989**, 5, 868.
- [53] V. V. Tsukruk, V. N. Bliznyuk, J. Hazel, D. Visser, M. P. Everson, *Langmuir* **1996**, 12, 4840.
- [54] J. Qu, W. C. Barnhill, H. Luo, H. M. Meyer, D. N. Leonard, A. K. Landauer, B. Kheireddin, H. Gao, B. L. Papke, S. Dai, *Adv. Mater.* **2015**, 27, 4767.
- [55] W. Guo, Y. Zhou, X. Sang, D. N. Leonard, J. Qu, J. D. Poplawsky, *ACS Appl. Mater. Interfaces* **2017**, 9, 23152.
- [56] W. C. Barnhill, J. Qu, H. Luo, H. M. Meyer, C. Ma, M. Chi, B. L. Papke, *ACS Appl. Mater. Interfaces* **2014**, 6, 22585.
- [57] J. Liu, J. K. Notbohm, R. W. Carpick, K. T. Turner, *ACS Nano* **2010**, 4, 3763.
- [58] J. E. Sader, J. W. M. Chon, P. Mulvaney, *Rev. Sci. Instrum.* **1999**, 70, 3967.
- [59] D. F. Ogletree, R. W. Carpick, M. Salmeron, *Rev. Sci. Instrum.* **1996**, 67, 3298.
- [60] B. Ravel, M. Newville, *J. Synchrotron Radiat.* **2005**, 12, 537.
- [61] M. P. Griffin, R. Gearba, K. J. Stevenson, D. A. Vanden Bout, A. Dolocan, *J. Phys. Chem. Lett.* **2017**, 8, 2764.

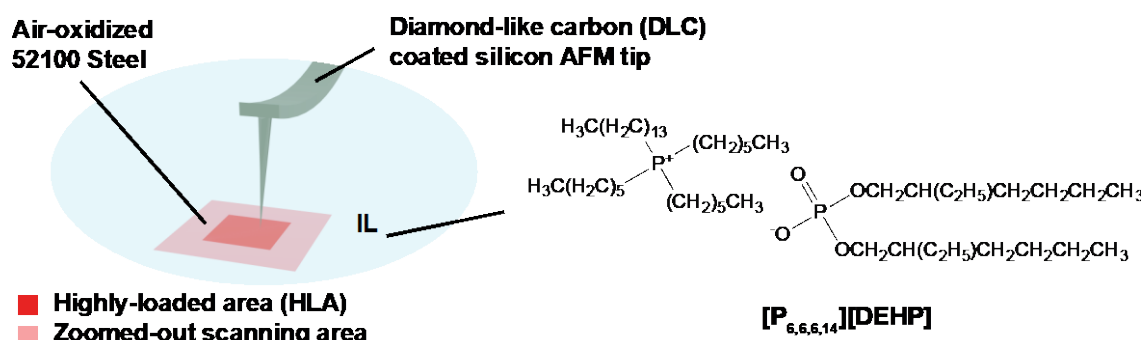


Figure 1. Schematic diagram of the *in situ* AFM test setup employed to evaluate the lubrication mechanism of [P_{6,6,6,14}][DEHP] IL together with the molecular structure of [P_{6,6,6,14}][DEHP].

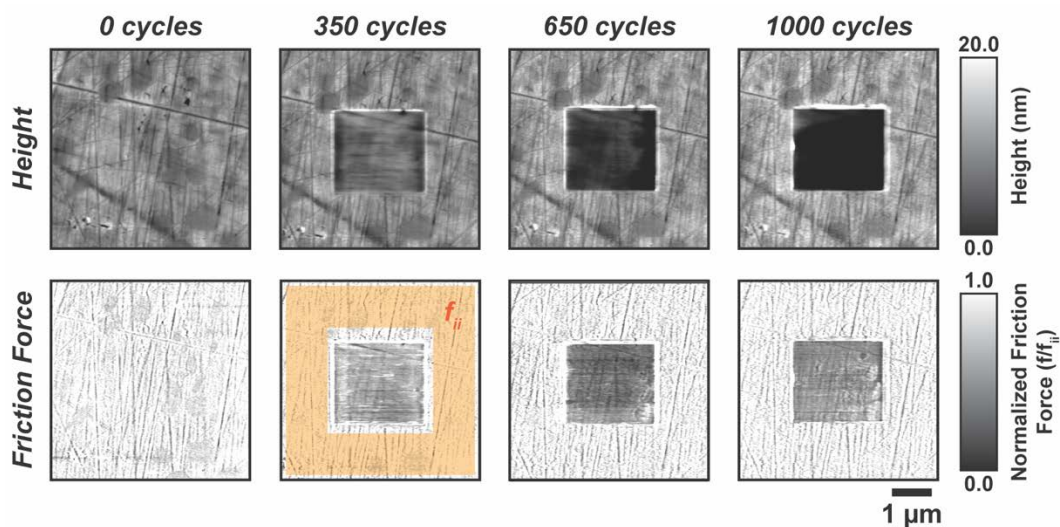


Figure 2. $5 \times 5 \mu\text{m}^2$ topographic (top row) and normalized friction force (bottom row) AFM images of an air-oxidized steel surface acquired using a diamond-like carbon (DLC)-coated silicon AFM tip immersed in $[\text{P}_{6,6,6,14}][\text{DEHP}]$. Above each column of images is the number of previously acquired $2 \times 2 \mu\text{m}^2$ scanning cycles at an applied pressure of $7.3 \pm 0.4 \text{ GPa}$. The friction force maps were normalized by the average friction force values (f_{ii}) in the RA.

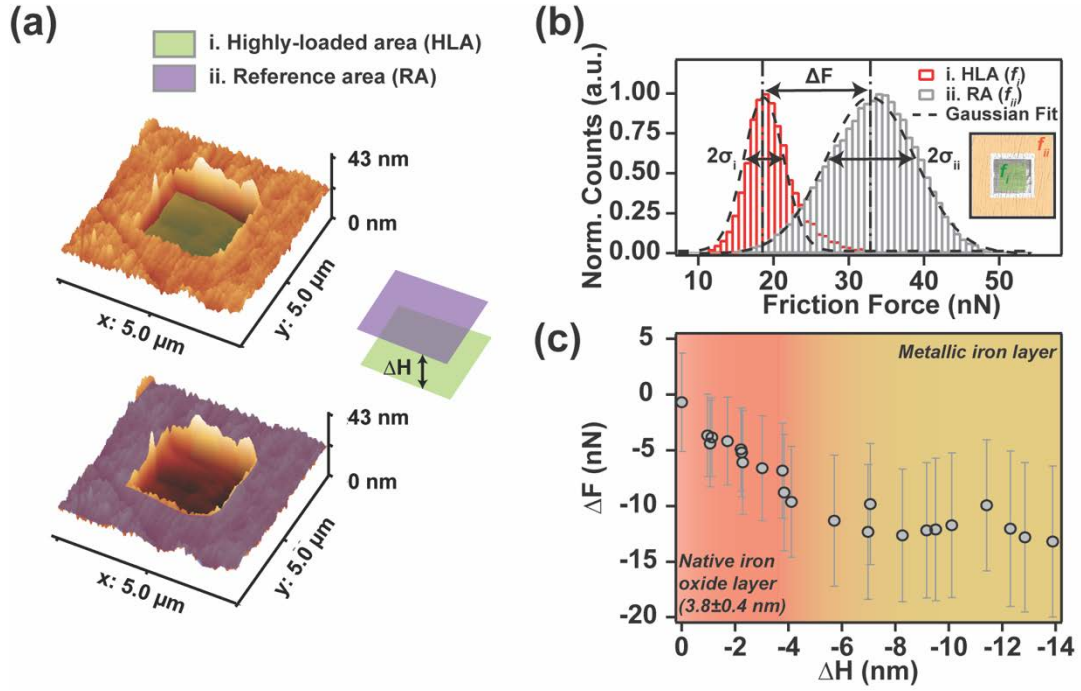


Figure 3. (a) 3D AFM topographic images showing the mean plane of the HLA and the mean plane of the RA, as well as the height difference (ΔH) between the two planes; (b) an example of friction force histograms obtained from selected regions of AFM friction maps, namely from the RA and the HLA. In the case of the example shown in (b), the friction map was obtained after scanning the central $2 \times 2 \mu\text{m}^2$ area for 1000 cycles at an applied pressure of 7.3 ± 0.4 GPa. The friction force histograms were fitted with Gaussian curves to quantify the evolution of the friction forces in the HLA relative to the ones in the RA (through the computation of the difference between the mean values of the force histograms, ΔF); (c) evolution of ΔF as a function of ΔH .

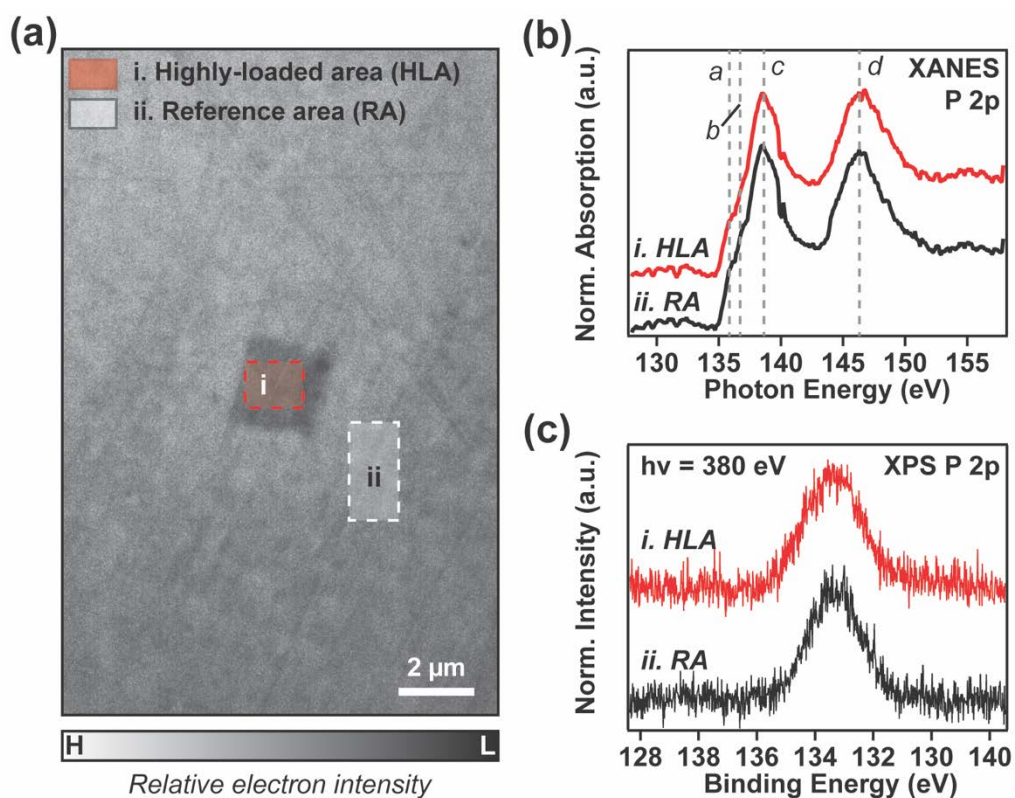


Figure 4. Synchrotron-based X-PEEM analyses of a steel surface after an AFM nanotribological experiment in $[\text{P}_{6,6,6,14}][\text{DEHP}]$ IL. (a) X-PEEM image acquired at 138 eV showing the area scanned at the HLA and RA; (b) XANES P 2p and (c) XPS P 2p spectra extracted from the HLA and RA. The X-PEEM spectra show the intensity per unit area from (a).

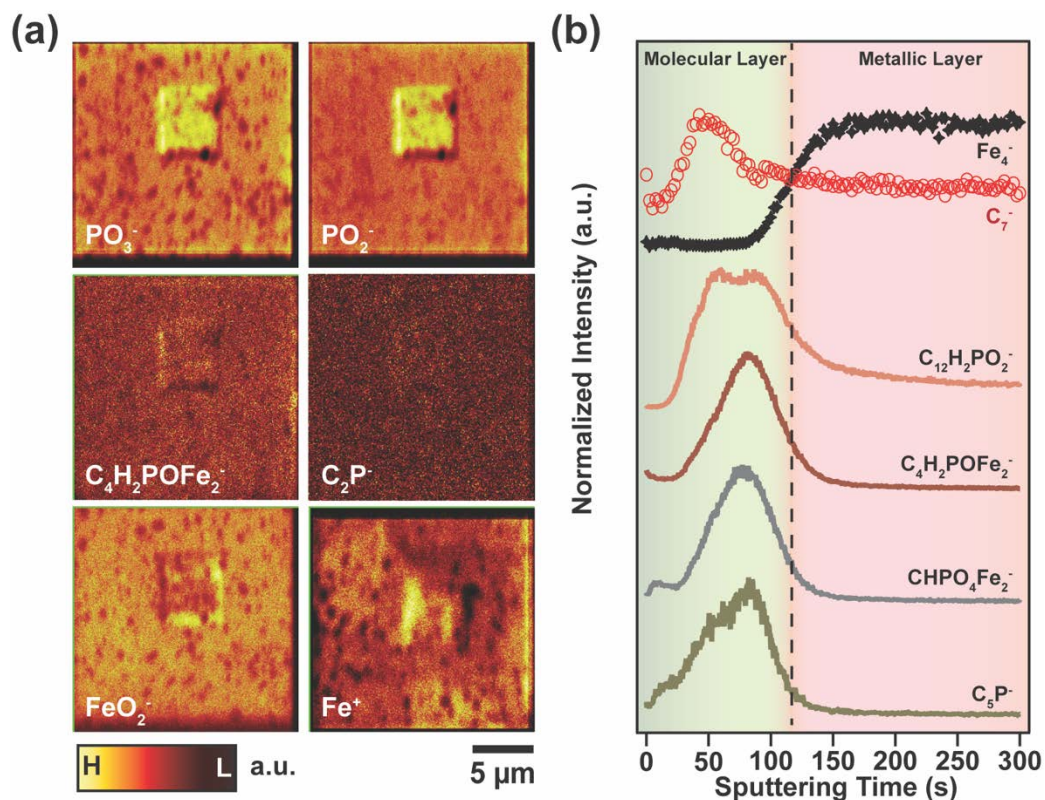


Figure 5. ToF-SIMS surface characterization of steel surfaces after AFM nanotribological experiments in $[P_{6,6,6,14}][DEHP]$ IL. (a) ToF-SIMS chemical maps showing the HLA and RA. The maps include lateral distribution of the fragments of PO_3^- , PO_2^- , $C_4H_2POFe_2^-$, FeO_2^- , C_2P^- , and Fe^+ , and (b) ToF-SIMS depth profiles of several ionized fragments obtained from a $100 \times 100 \mu m^2$ area on a steel reference sample left in contact with $[P_{6,6,6,14}][DEHP]$ IL at $111^\circ C$ for the same duration of a typical AFM nanotribological tests, but without being scanned by AFM tips.

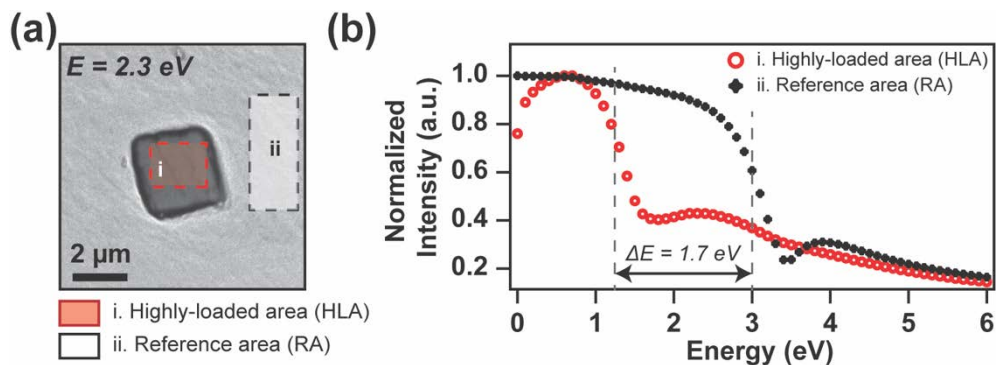


Figure 6. LEEM analysis of a steel surface after an AFM nanotribological experiment in $[\text{P}_{6,6,6,14}][\text{DEHP}]$ IL. (a) LEEM image taken at the ejected electron energy of 2.3 eV, showing the contrast between the area scanned by the AFM tip at high load (HLA) and the surrounding area; (b) reflected electron intensity versus electron energy curves extracted from the HLA and the RA highlighted in (a).

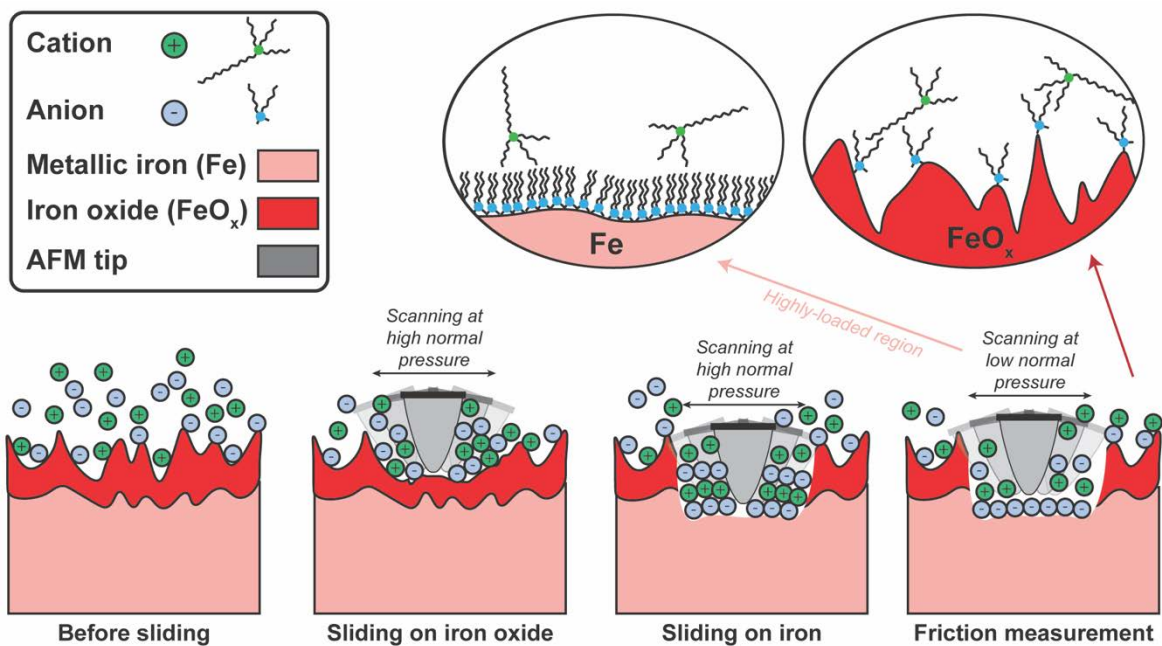


Figure 7. Schematic model for the lubrication mechanism of [P_{6,6,6,14}][DEHP] IL on air-oxidized steel. The magnified schematics represent the different surface adsorption configurations of the [DEHP] anions adsorbed on iron oxide and metallic iron.

Trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ($[P_{6,6,6,14}][DEHP]$) has been proved to be an excellent lubricant additive on steel. For the first time, *in situ* nanotribological tests and *ex situ* laterally-resolved surface characterizations are combined to establish a phenomenological model on IL lubrication, in which the friction reduction property of $[P_{6,6,6,14}][DEHP]$ is ascribed to the different adsorption configurations of their $[DEHP]$ anions on iron oxide and metallic iron.

Keyword: lubrication

Zixuan Li, Andrei Dolocan, Oscar Morales-Collazo, Jerzy T. Sadowski, Hugo Celio, Robert Chrostowski, Joan F. Brennecke, and Filippo Mangolini*

Lubrication Mechanism of Phosphonium Phosphate Ionic Liquid in Nanoscale Single-Asperity Sliding Contacts

