Supporting information for

Lubrication Mechanism of a Strong Tribofilm by Imidazolium Ionic Liquid

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0.1 mmol 1-Methylimidazole (8.21 g) and 0.1 mol (3-Chloropropyl) trimethoxysilane (19.87 g) were dissolved in 120 mL anhydrous DMF. The solution was stirred at 80 °C under argon atmosphere for 48 h. The product was extracted with anhydrous diethy ether, followed by drying in a vacuum oven at 80 °C overnight. It was then collected and denoted as imidazolium ionic liquid (ImIL). The $^1$H NMR and MS spectra of the product are in Figure S1-1 and S1-2 respectively.

Figure S1-1. The $^1$H NMR spectrum of ImIL one week after its synthesis.

ImIL is stable in ambient environment. Its chemical structure soon after and one week after its synthesis, as confirmed by $^1$H NMR, are identical (the latter in Figure S1-1). Note that small amount of impurities exist in ImIL. For example, the peak around 3.16 ppm can be attributed to the water in the solution, as DMSO-d6 absorbs water strongly. The peaks around 2.92 ppm, and 2.74 ppm can be ascribed to residual from the solvent DMF used for ImIL synthesis. Note that these impurities are common in organic synthesis and are unlikely to affect our conclusion as their concentrations are low.
Figure S1-2. The mass spectrum of IL

The peak at m/e 245.1315 is ascribed to ImIL. The two satellite peaks at 246.1336 and 247.1306 in the mass spectrum presented in Figure S1-2 are from the isotopes, $^{13}$C and $^{18}$O/$^{30}$Si, which are common in organic synthesis. The peaks around 231.1158, 217.1004, and 203.0851 in the mass spectrum are because little amount of ImIL was partially hydrolysed. Note that hydrolyzation of ImIL may promote the formation of the brush structure shown in Figure 10e. Thus, these byproducts will not affect our tribological performance and conclusion.
S2 – Average friction coefficients and wear track width on worn discs obtained for all tested lubricants

Figure S2. The average friction coefficients and wear track width of wear discs obtained with and without ImIL in (a) PEG on steel surface; (b) 1,4-butandiol on steel surface; (c) PEG on DLC surface
S3 – Wear scars produced on DLC coated steel in PEG and on steel in 1,4-butandiol

|                      | White light interferometric images | Profile orthogonal to the rubbing direction | Profile parallel to the rubbing direction |
|----------------------|-----------------------------------|-------------------------------------------|------------------------------------------|
| (a) Neat PEG on DLC  | ![Image](image1)                  | ![Graph](graph1)                          | ![Graph](graph2)                         |
| (b) 5% ImIL in PEG on DLC | ![Image](image2)                  | ![Graph](graph3)                          | ![Graph](graph4)                         |
| (c) BD on steel      | ![Image](image3)                  | ![Graph](graph5)                          | ![Graph](graph6)                         |
| (d) 5% IL in BD on steel | ![Image](image4)                  | ![Graph](graph7)                          | ![Graph](graph8)                         |

Figure S3. Profiles of wear scars formed in (a) neat PEG on DLC surface; (b) 5 wt% ImIL containing PEG on DLC surface; (c) neat 1,4-butandiol on steel surface; (d) 5 wt% ImIL 1,4-butandiol on steel surface.
S4 – Effectiveness of ImIL in PEG on lubrication steel-steel contacts

Figure S4-1. The friction coefficient and ECR of steel-steel contacts lubricated by 1,3-propanediol with and without ImIL

Figure S4-2. The optical images of the wear tracks on steel discs lubricated with (a) neat 1,3-propanediol; (b) 5 wt% IL containing 1,3-propanediol
S-5 Molecular Dynamic simulation

All-atom Molecular dynamic (MD) simulations were carried out with Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). A 70 Å × 70 Å × 70 Å cell was constructed, as shown in Figure S5-1a. It was randomly filled with 300 PEG molecules (Mw = 414 g/mol) and 300 ImIL pairs, resulting in an initial liquid density at 0.95 g/cm³. The liquid cell was confined with two walls made of 8 layers of FeO. Each wall, with thickness of 17 Å, was composed of 2304 Fe atoms and 2304 O atoms. Periodic boundary conditions were applied on the x- and y- directions. The OPLS all-atom force field was employed to model the behaviour of PEG and ionic liquid⁷⁻⁹, while the force field proposed by Cygan et al. was employed for FeO⁶,¹⁰. The whole system was energy-minimized before compression. Then, the temperature control was applied to both the walls and liquid at 313 K with a Noser-Hoover thermostat. A normal force was imposed on top wall uniformly, giving a pressure of 500 MPa. The simulation was run for 2 ns with timestep of 0.5 fs to reach equilibrium.

Figure S5-1. (a) All-atom MD simulation of 300 PEG molecules and 300 IL pairs confined between FeO walls. The molecular structure of (b) ImIL, and (c) PEG.
Figure S5-2. (a) The variation of liquid density during the compression MD simulation, (b) The number density profiles in z of oxygen, silicon and nitrogen in ImIL at equilibrium.

MD simulations were used to examine the conformation of ImIL in PEG on iron oxide surface. The solution is under compression (uniform pressure of 500 MPa). At equilibrium, the density of the solution reaches a stable value at 1.13 g/cm$^3$ (Figure S5-2a). The number density profiles of nitrogen (N), silicon (Si) and oxygen (O) of ImIL along the z direction are shown in Figure S5-2b. Notably, there are two peaks at 78 Å and 18 Å in oxygen and silicon profile. In contrast, the N atoms showed a much more uniform distribution along the z axis. This implies that the concentration of IL is higher concentration at the solid-liquid interface. This reveals that IL was anchored on the iron oxide (steel) surface by the oxygen-containing side instead of the imidazolium ring.
S-6 XPS spectra of steel wear scars formed in ImIL containing 1,4-butanediol

Figure S6. XPS spectra of wear tracks lubricated by neat 1,4-butanediol and 5 wt% ImIL in 1,4-butanediol.
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