

# Lithium-based ionic liquids as novel lubricant additives for multiply alkylated cyclopentanes (MACs)

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**Abstract:** Two lithium-based ionic liquids (ILs, L-C3N3, and L-P3N3) were synthesized and evaluated as novel lubricant additives for multiply alkylated cyclopentanes (MACs). They were found to be approximately 1.0% soluble in MACs at room temperature (RT), whereas traditional ILs, such as 1-ethyl-3-methylimidazolium tetrafluoroborate (L-B102), 1-hexyl-3-methylimidazolium hexafluorophosphate (L-P106), and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (L-F102), could not be dissolved in this base oil. Friction tests indicated that these ILs exhibit excellent friction-reducing and anti-wear properties both at RT and at 100 °C. They can improve the tribological properties of MACs at RT to a greater extent than the commonly used lubricant zinc dialkyldithiophosphate (T204), even at a concentration of 0.1%. The load ramp test showed that MACs with L-C3N3 and L-P3N3 also exhibit high load-carrying capabilities. Scanning electron microscope (SEM) and X-ray photoelectron spectrometer (XPS) results indicated that physical adsorption and complex tribochemical reactions occurred between the ILs and metal surfaces during the sliding process, thereby forming a surface protective film that significantly contributed to the excellent tribological properties of the new ILs.

**Keywords:** ionic liquids; sym-triazine; cyclotriphosphazene; additives; multiply alkylated cyclopentanes; tribology

## 1 Introduction

Multiply alkylated cyclopentanes (MACs) are composed of one cyclopentane ring with two to five alkyl groups substituted on the ring. In recent years, numerous studies focused on the application of MACs in patterned lubricant films for microelectromechanical systems (MEMS) have appeared in the literature due to their outstanding physical, and chemical properties, which include excellent viscosity properties, good thermal stability, high flexibility and very low volatility [1–5]. Taking advantage of these characteristics, researchers expect to expand the use of MACs as liquid lubricants. However, neat MACs cannot satisfy the requirements of practical applications in developing modern technologies. Lubricating oils are typically

optimized through additive technology and the development of new additives suitable for use with MACs is important in improving their tribological properties. During the last decade, ionic liquids (ILs) have been rapidly developed as new types of lubricant or lubricant additives due to their excellent tribological performance and unique physicochemical properties, which satisfy the requirements of high-performance lubricants [6–9]. The structures of commonly used IL lubricants or additives are based on bulky asymmetrical cations such as ammonium, phosphonium, pyridinium and imidazolium cations. The choices of anions include  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$  (TFSI<sup>-</sup>), and  $(\text{CF}_3\text{CF}_2)_3\text{PF}_4^-$  (FAP<sup>-</sup>) [10]. However, these IL lubricants have some disadvantages that limit their applications. For example, these ILs suffer some significant cost drawbacks related to their synthesis and purification and they are insufficiently soluble to be used as lubricant additives in base oils. In our previous

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work, we reported a new class of IL additives based on lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) and glymes or synthetic esters [11, 12]. The weakly Lewis-acidic cations,  $[\text{Li}(\text{glyme})]^+$  and  $[\text{Li}(\text{synthetic ester})]^+$ , can be obtained by the coordination of  $\text{Li}^+$  (as a Lewis acid) with glyme and synthetic ester (as Lewis bases), respectively. The  $[\text{Li}(\text{glyme})]^+$  and  $[\text{Li}(\text{synthetic ester})]^+$  can then form ILs,  $[\text{Li}(\text{glyme})]\text{TFSI}$  and  $[\text{Li}(\text{synthetic ester})]\text{TFSI}$ , with the weakly Lewis-basic anion TFSI<sup>-</sup> [12, 13]. These ILs are obtained only when an appropriate molar ratio of LiTFSI and glymes or synthetic esters are blended together, which can significantly reduce the costs associated with IL preparation.

Based on a similar concept, we synthesized two novel sym-triazine- or cyclotriphosphazene-functionalized and lithium-based ILs in this work. The tribological behaviors of these ILs in MACs were determined. The results show that they have excellent extreme-pressure, friction-reducing and anti-wear properties when used as lubricant additives for MACs. As far as we know, this work represents the first example of the use of ILs as lubricant additives in MACs.

## 2 Experimental

### 2.1 Chemicals and synthesis of the ILs

The chemical structures of the compounds used for preparing ILs are given in Fig. 1. The compounds, tri(methoxyethoxyethoxyethoxy)triazine ( $\text{C}_3\text{N}_3(\text{OR})_3$ ) and hexa(methoxyethoxyethoxyethoxy)cyclotriphosphazene ( $\text{P}_3\text{N}_3(\text{OR})_6$ ), were synthesized according to the method described in the literature [14]. Chlorotriazine ( $\text{C}_3\text{N}_3\text{Cl}_3$ ) and hexachlorocyclotriphosphazene ( $\text{P}_3\text{N}_3\text{Cl}_6$ ) were purchased from Alfa Aesar. Triglycol monomethyl ether and LiTFSI were purchased from J&K. The zinc dialkyldithiophosphate package (T204) was purchased from LuBoRun Lanzhou LanLian Additive Co., Ltd. The MACs was synthesized in our laboratory. All other chemicals utilized in this work were AR grade. We prepared the ILs, L-C3N3, and L-P3N3, by blending an appropriate molar ratio of  $\text{C}_3\text{N}_3(\text{OR})_3$  or  $\text{P}_3\text{N}_3(\text{OR})_6$  and LiTFSI together. The mixtures were subsequently stirred at moderate speed at approximately 80 °C until homogeneous liquids formed. The  $\text{C}_3\text{N}_3(\text{OR})_3/\text{LiTFSI}$  and  $\text{P}_3\text{N}_3(\text{OR})_6/\text{LiTFSI}$  molar ratios were 1.0:3.0 and 1.0:6.0, respectively.

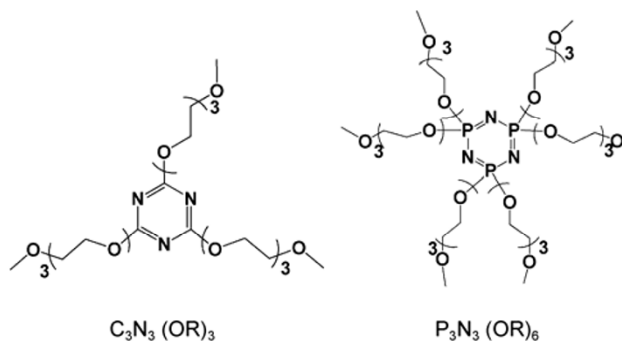


Fig. 1 Molecular structures of  $\text{C}_3\text{N}_3(\text{OR})_3$  and  $\text{P}_3\text{N}_3(\text{OR})_6$ .

### 2.2 Characterization

The coordination between  $\text{Li}^+$  and  $\text{CH}_2\text{-O}$  groups in the ILs was confirmed by Fourier transform infrared spectrometry (FTIR). The FTIR spectra were recorded on a Nicolet iS10 FTIR spectrometer between 4,000  $\text{cm}^{-1}$  and 400  $\text{cm}^{-1}$  with a resolution of 1  $\text{cm}^{-1}$ . A droplet of liquid sample was spread onto a dry KBr pellet for the infrared (IR) spectroscopic measurements. The thermal behaviors of the ILs were measured on a STA 449 C Jupiter® instrument for the simultaneous thermogravimetry and differential scanning calorimetry (TG–DSC) measurements performed at a heating rate of 10 °C/min in air. The morphologies of the worn surfaces were obtained using a JSM-5600LV scanning electron microscope (SEM). To explore the lubricating mechanism of the lubricants, we performed X-ray photoelectron spectrometer (XPS) measurements on a K-Alpha XPS equipped with an Al-K $\alpha$  excitation radiation source. The binding energies of the target elements were determined at a pass energy of 50.0 eV.

### 2.3 Friction and wear tests

The tribological properties of MACs with different additives for steel/steel contact was evaluated with an Optimol SRV-IV oscillating reciprocating friction and wear tester at room temperature (RT) and at 100 °C. To achieve contact between the frictional pairs, the upper running ball (AISI 52100 steel, 10 mm in diameter, hardness of approximately 59–61 HRC) was pressed against the lower stationary disc (AISI 52100 steel,  $\varnothing$  24 mm  $\times$  7.9 mm, hardness of approximately 63–67 HRC) and mechanically reciprocated at a given frequency and displacement. The friction and wear tests

in this experiment were conducted at an amplitude of 1 mm, a frequency of 25 Hz, a test duration of 30 min and a relative humidity of 20%–50%. Prior to the friction and wear tests, a moderate amount of lubricant was placed onto the ball–disc contact area. The corresponding friction curves were recorded automatically by the SRV test rig. The wear volume losses from lower discs were measured using a MicroXAM-3D non-contact surface mapping microscope profilometer.

### 3 Results and discussion

#### 3.1 Spectroscopic characterization

Figure 2 shows the IR spectra of the C–H stretching mode of the coordinated ILs. The corresponding stretching modes of  $C_3N_3(OR)_3$  and  $P_3N_3(OR)_6$  are shown for comparison. As evident in Fig. 2, the strong bands at  $2,883\text{ cm}^{-1}$  in the IR spectra of  $C_3N_3(OR)_3$  and  $P_3N_3(OR)_6$  are attributed to the C–H symmetric and anti-symmetric stretching modes. When lithium salts were introduced into  $C_3N_3(OR)_3$  and  $P_3N_3(OR)_6$ , however, the corresponding bands in L-C3N3 and L-P3N3 changed significantly. The bands were split into two peaks [15], appearing at  $2,900\text{ cm}^{-1}$  and  $2,987\text{ cm}^{-1}$ . This split means that some of the O atoms in the  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$  groups coordinate strongly with  $\text{Li}^+$ , which results in a shift of the C–H stretching band to  $2,987\text{ cm}^{-1}$ , whereas other C–H bonds far from the lithium-coordinated oxygen are only weakly affected. These results confirm the IL formation

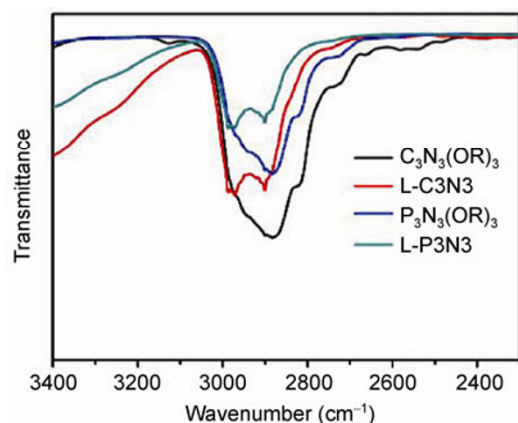


Fig. 2 FTIR spectra of the C–H stretching mode of the ILs.

between  $C_3N_3(OR)_3$  or  $P_3N_3(OR)_6$  and LiTFSI via  $\text{Li}^+\text{--O}$  coordination.

#### 3.2 Solubility and thermal properties

The solubility tests showed that L-C3N3 and L-P3N3 are approximately 1.0% *w/w* soluble in MACs. Even after the samples were stored for one month, their solubility did not change. This stability gives L-C3N3 and L-P3N3 a strong advantage over conventional ILs, such as 1-ethyl-3-methylimidazolium tetrafluoroborate (L-B102), 1-hexyl-3-methylimidazolium hexafluorophosphate (L-P106) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (L-F102), which cannot be dissolved in this base oil and are rarely used as lubricant additives in MACs.

Figure 3 presents the thermogravimetry (TG) curves for the lubricants; the corresponding results are listed in Table 1. The curves indicate that the decomposition temperatures at different weight-loss percentages of MACs with 1.0% L-C3N3 and 1.0% L-P3N3 are higher than those of pure MACs. For example, the decomposition temperature that accompanies a 10% weight loss in the MACs increased dramatically from  $245.9\text{ }^\circ\text{C}$  to  $267.9\text{ }^\circ\text{C}$  and  $270.2\text{ }^\circ\text{C}$  after 1.0% L-C3N3 and 1.0% L-P3N3, respectively, were added. Moreover, the onset decomposition temperature of MACs increased from  $238.0\text{ }^\circ\text{C}$  to  $260.0\text{ }^\circ\text{C}$  and  $264.5\text{ }^\circ\text{C}$  when 1.0% L-C3N3 and 1.0% L-P3N3, respectively, were added. Thus, the ILs can obviously improve the decomposition temperatures of MACs, which demonstrates that the ILs are suitable for use as additives in MACs with respect to their thermal stability.

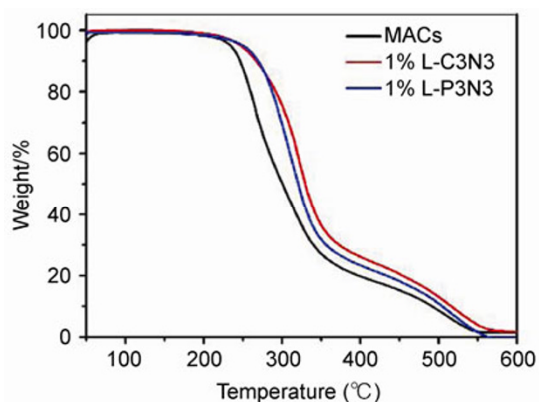


Fig. 3 TG curves of the compounds: MACs and MACs with 1% ILs.

**Table 1** The thermal properties of the compounds.

Compound	TG temperature (°C) per weight loss			Onset decomposition temperature (°C)
	10%	20%	50%	
MACs	245.9	259.4	300.9	238.0
1.0% L-C3N3	267.9	292.9	330.4	260.0
1.0% L-P3N3	270.2	287.7	320.2	264.5

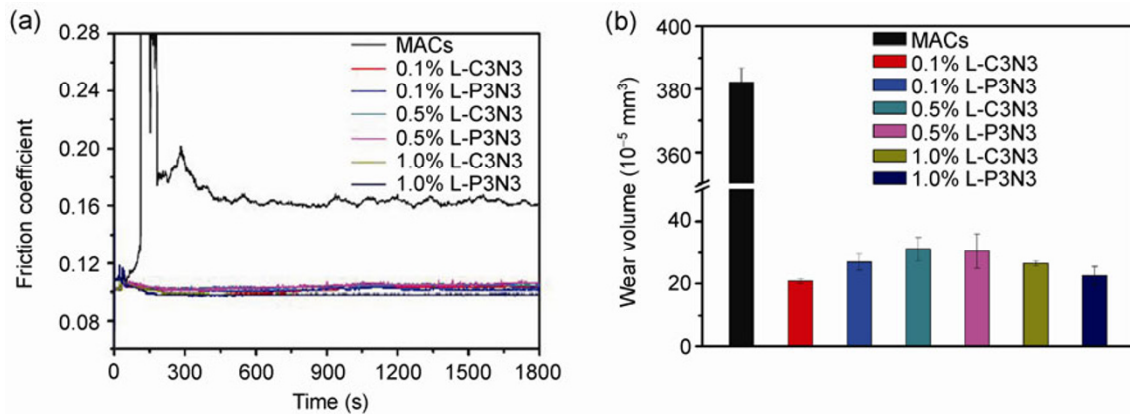
### 3.3 Friction and wear behaviors

#### 3.3.1 Room-temperature tests

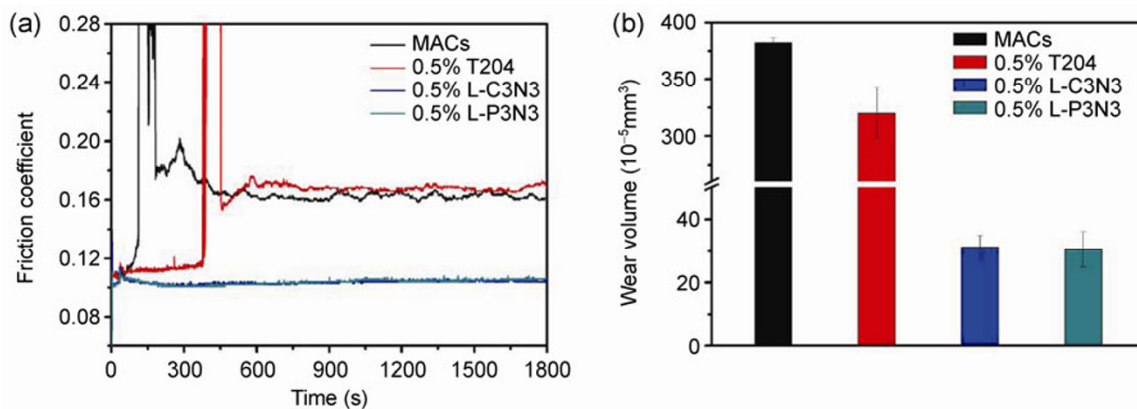
Figure 4 shows the SRV test results for a load of 300 N applied at RT for steel/steel contact lubricated by MACs with different concentrations of L-C3N3 and L-P3N3. As shown in Fig. 4(a), the pure MACs exhibits relatively longer running-in time and larger friction

coefficients, whereas L-C3N3 and L-P3N3 at concentrations from 0.1% to 1.0% exhibit similar lower and more stable friction coefficients. As shown in Fig. 4(b), the wear volume losses of the steel discs lubricated by L-C3N3 and L-P3N3 at concentrations from 0.1% to 1.0% are all smaller than that of steel discs lubricated by pure MACs. The addition of 0.1% L-C3N3 improved the anti-wear property of the base oil by a factor of more than 18. This improvement indicates that the ILs, L-C3N3, and L-P3N3, can significantly improve the tribological behavior of MACs at RT and that the optimized additive concentration may be as low as 0.1%.

The changes in friction coefficients and wear volume losses of sliding discs under lubrication of 0.5% L-C3N3, 0.5% L-P3N3 and 0.5% T204 (for comparison) are displayed in Fig. 5. In Fig. 5(a), 0.5% T204 exhibits a friction behavior comparable to that of the base oil. Both



**Fig. 4** Evolution of the friction coefficients (a) and the wear volume losses (b) for steel discs lubricated by MACs with different concentrations of L-C3N3 and L-P3N3 at RT (load = 300 N, stroke = 1 mm, frequency = 25 Hz, duration = 30 min).



**Fig. 5** Evolution of the friction coefficients (a) and the wear volume losses (b) for steel discs lubricated by different lubricants at RT (load = 300 N, stroke = 1 mm, frequency = 25 Hz, duration = 30 min).

the 0.5% T204 sample and the base oil have relatively long running-in times with large friction coefficients ( $> 0.16$ ), whereas the running-in times for 0.5% L-C3N3 and 0.5% L-P3N3 are dramatically shortened. The friction coefficients of 0.5% L-C3N3 and 0.5% L-P3N3, which are substantially lower than those of MACs and 0.5% T204, are similar and remain very stable. The wear volume results in Fig. 5(b) show that 0.5% L-C3N3 and 0.5% L-P3N3 exhibit anti-wear abilities superior to that of 0.5% T204. The results indicate that these two ILs have excellent friction-reducing and anti-wear properties when used as lubricant additives for MACs and that their tribological properties are far better than that of the normally used additive T204.

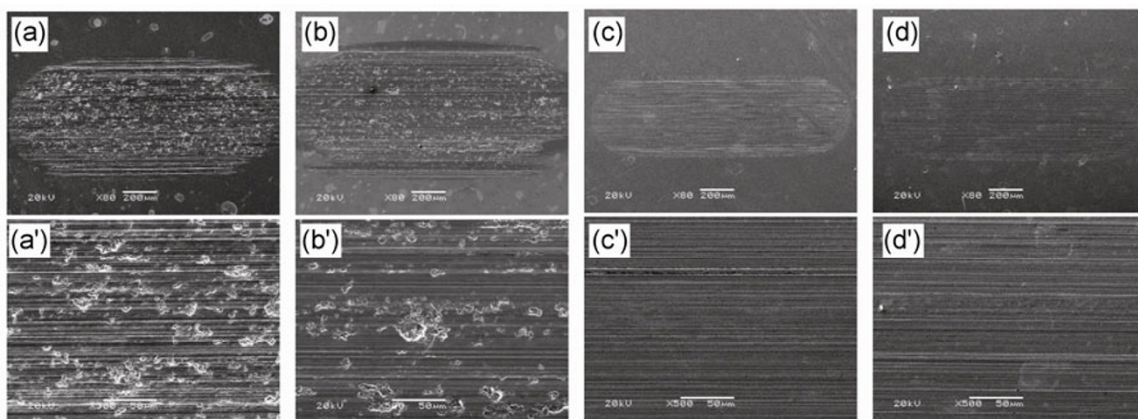
The SEM micrographs of the worn surfaces of the steel discs lubricated by MACs and MACs with the three additives at RT are shown in Fig. 6. The figure clearly shows that the worn surfaces under the lubrication of pure MACs and MACs with 0.5% T204 are characterized by severe scuffing. Some deep and narrow grooves are visible in the micrographs (Figs. 6(a), (a'), (b), and (b')); these grooves correspond to severe adhesive wear and indicate that T204 is not an effective additive in MACs for the lubrication of steel/steel contact. Contrary to the previously discussed results, Figs. 6(c), (c'), (d), and (d') show that the wear scars on the steel discs lubricated by 0.5% L-C3N3 and 0.5% L-P3N3 are smaller than those lubricated by pure MACs and by MACs with 0.5% T204 and show fewer and smoother grooves. Moreover, adhesive wear and

scuffing was greatly alleviated during the sliding process. These results are consistent with previously measured wear volume results and indicate that L-C3N3 and L-P3N3, when used as additives in MACs, can significantly increase the steel/steel contact wear resistance.

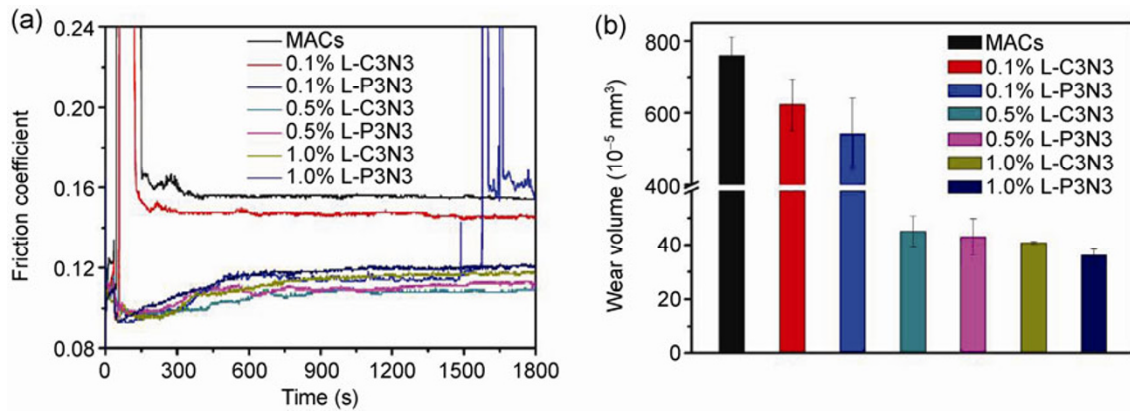
### 3.3.2 High-temperature tests

High-temperature tests were performed to study the friction behaviors of the IL additives in MACs. The results are shown in Fig. 7. Figure 7(a) shows the evolution of the friction coefficient as the IL concentration was increased. When the concentration of L-C3N3 was 0.1%, the IL had no obvious effect on the friction behavior of the base oil at 100 °C. The friction observed with 0.1% L-P3N3 was very stable and low at the beginning of the test, but became large during the last few minutes of the test. When the IL concentration was greater than 0.5%, the running-in time was dramatically shortened, concomitant with a stable and low friction coefficient.

The wear volume results (Fig. 7(b)) are consistent with the friction coefficient results. The 0.1% L-C3N3 and 0.1% L-P3N3 lubricants showed high wear volume values, whereas the MAC with 0.5% L-C3N3 and 0.5% L-P3N3 exhibited anti-wear properties almost 17 times greater than those of the MAC that did not contain an IL. The results indicate that the addition of ILs significantly improves the tribological properties of MACs at 100 °C.



**Fig. 6** SEM micrographs showing the morphologies of the worn surfaces lubricated by different lubricants at RT: (a, a') MACs, (b, b') 0.5% T204, (c, c') 0.5% L-C3N3, and (d, d') 0.5% L-P3N3 (magnification: top row, 80 $\times$ ; bottom row, 500 $\times$ ; load = 300 N; stroke = 1 mm; frequency = 25 Hz; duration = 30 min).

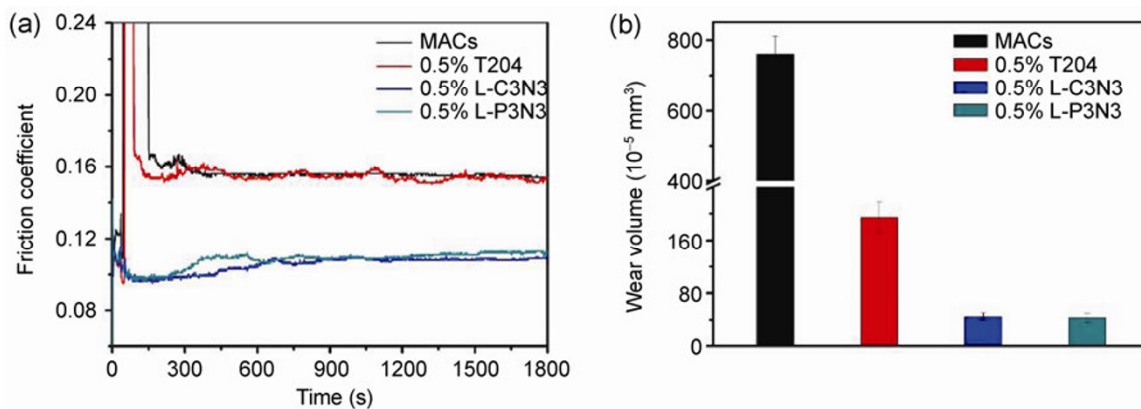


**Fig. 7** Evolution of the friction coefficients (a) and the wear volume losses (b) for steel discs lubricated by MACs with different concentrations of L-C3N3 and L-P3N3 at 100 °C (load = 300N, stroke = 1 mm, frequency = 25 Hz, duration = 30 min).

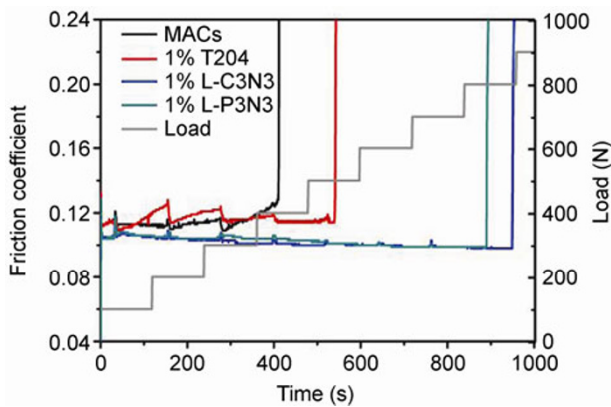
Figure 8 shows the variation of the friction coefficients and the wear volume losses of the sliding discs under lubrication of MACs and MACs plus 0.5% T204, 0.5% L-C3N3, and 0.5% L-P3N3 at 100 °C. Fig. 8(a) shows that the friction behavior of the 0.5% T204 sample is similar to that of MACs: both exhibited high friction coefficient values during the whole testing process. However, the novel ILs exhibited excellent tribological behaviors that are effective in reducing the friction of MACs. With all of the investigated IL additives, the wear volume losses were smaller than that of pure MACs (Fig. 8(b)). The MACs with 0.5% L-C3N3 and 0.5% L-P3N3 exhibited better anti-wear properties than the MACs with 0.5% T204. The results indicate that L-C3N3 and L-P3N3 exhibit excellent tribological performance at 100 °C and better lubricating abilities than commonly used T204.

### 3.3.3 Load ramp test

The load-carrying capabilities of the ILs were measured by load ramp tests. The corresponding results are shown in Fig. 9. The tests were conducted from 100 N up to 800 N in 100-N intervals at RT with a 2-min test duration for each load. During the test, the friction coefficient of MACs was extremely high when the load was increased to 400 N, which is unsatisfactory. With respect to T204, the addition of T204 to a concentration of 1.0% improved the load-carrying capability of MACs by only 100 N, with stoppage at 500 N. In contrast, the two synthetic ILs, L-C3N3 and L-P3N3, exhibited lower and much more stable friction coefficients with increasing load compared with 1.0% T204 and the neat oil when added to MACs to a concentration of 1.0%. The frictional behaviors of MACs with 1.0%



**Fig. 8** Evolution of the friction coefficients (a) and the wear volume losses (b) for steel discs lubricated by different lubricants at 100 °C (load = 300N, stroke = 1 mm, frequency = 25 Hz, duration = 30 min).



**Fig. 9** Evolution of the friction coefficients with time during a load ramp test from 100 N to 900 N for MACs with different additives at RT (stroke = 1 mm, frequency = 25 Hz).

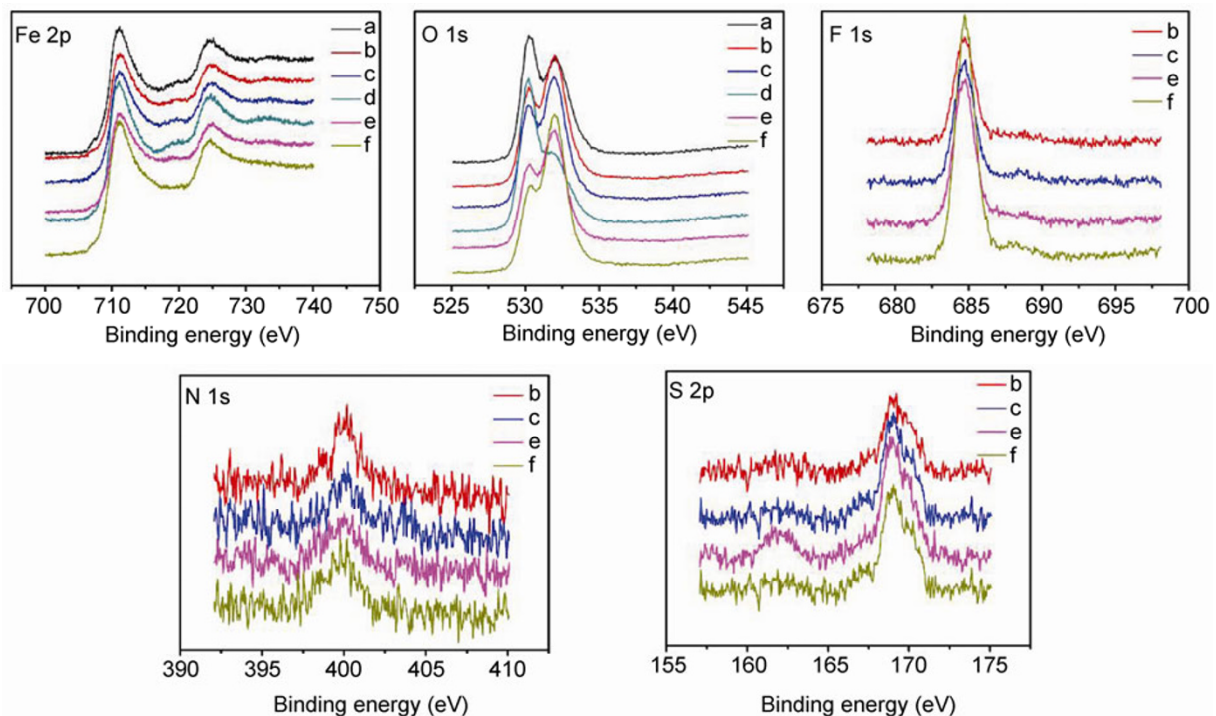
L-C3N3 and 1.0% L-P3N3 were quite similar, and both exhibited good lubricity until the load was increased to 900 N. We therefore concluded that the synthetic ILs have good friction-reducing and high load-carrying capabilities.

### 3.4 Surface analyses

The previously discussed test results indicate that the IL additives in MACs possess excellent tribological

properties for steel/steel contact at both RT and high temperature (100 °C). From a mechanistic point of view, these properties can be attributed to their heterocyclic skeletal cation and the TFSI<sup>-</sup> anion. We hypothesize that, during the sliding process, the ILs can be easily adsorbed onto the metal surfaces and that a tribochemical reaction easily occurs between the ILs and metal surfaces to form a surface protective film that contributes significantly to the excellent tribological properties of the new ILs.

To test this hypothesis, we performed XPS analysis of the worn surfaces lubricated by base oil, 0.5% L-C3N3 and 0.5% L-P3N3. The XPS spectra are shown in Fig. 10. The spectra indicate that the binding energies of Fe, O, F, and N of the worn surfaces lubricated by 0.5% L-C3N3 and 0.5% L-P3N3 at RT and 100 °C are similar to each other and that no characteristic peak of P 2p was detected on the worn steel lubricated by 0.5% L-P3N3. These results suggest that the additives on the worn surface underwent similar tribochemical reactions both at RT and at 100 °C. The XPS spectral peaks of Fe 2p appear at 711.2 eV and 724.9 eV, and the O 1s peaks appear at 530.2 eV and 532.0 eV, which may be ascribed to FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, FeOOH,



**Fig. 10** XPS spectra of the worn surfaces lubricated by different lubricants: (a) MACs at RT, (b) 0.5% L-C3N3 at RT, (c) 0.5% L-P3N3 at RT, (d) MACs at 100 °C, (e) 0.5% L-C3N3 at 100 °C, and (f) 0.5% L-P3N3 at 100 °C.

Fe(OH)O, FeSO<sub>4</sub> or Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> [16]. The O1s peaks for the worn steel surfaces lubricated by MACs at 530.2 eV are higher than that at 532.0 eV. On the contrary, for those steels lubricated by 0.5% L-C3N3 and 0.5% L-P3N3, the O1s peaks at 530.2 eV are lower than the peak at 532.0 eV. These results indicate that FeSO<sub>4</sub> or Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> was generated in greater abundance than FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, FeOOH or Fe(OH)O on the worn steel surfaces lubricated by 0.5% L-C3N3 and 0.5% L-P3N3. No characteristic peaks were detected in the F 1s, N 1s, and S 2p XPS spectra of the worn steel surface lubricated by pure MACs (not shown in Fig. 10). However, the F 1s XPS spectra of worn steel surfaces lubricated by 0.5% L-C3N3 and 0.5% L-P3N3 at RT and 100 °C contained obvious peaks at 684.8 eV, which indicates the presence of fluorine anions, possibly due to the formation of FeF<sub>2</sub> and/or FeF<sub>3</sub> (according to the binding energy of Fe 2p of 711.2 eV) [16–18]. Similarly, peaks appear at 400.2 eV in the N 1s XPS spectra; these peaks possibly correspond to nitrogen oxide [18, 19]. The peaks of S2p mainly appear at 169.0 eV and can be identified as FeSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and/or –SO<sub>2</sub> [16, 20].

With respect to the steel lubricated by 0.5% L-C3N3 at 100 °C, an additional S 2p peak appears at 161.9 eV, which possibly corresponds to FeS [16, 20]. Thus, under the experimental conditions, a precise determination of the exact tribological protective film species on the worn steel surfaces is difficult. However, on the basis of the previously discussed data, we minimally conclude that, under the collective effects of high pressure, exoelectron emission and frictional heating, complicated tribochemical reactions occur on the steel surfaces lubricated by 0.5% L-C3N3 and 0.5% L-P3N3 during the friction process, accompanied by the generation of a surface protective film composed of nitrogen oxide, sulfate, FeF<sub>2</sub>, FeF<sub>3</sub> or FeS. Thus, in this case, the excellent tribological properties are attributed to the polarity-induced physical adsorption films of the ILs on the surfaces and, more importantly, further tribochemical reaction films of the ILs with the sliding metallic surfaces.

## 4 Conclusions

Two sym-triazine- and cyclotriphosphazene-functionalized ILs, L-C3N3 and L-P3N3, were

synthesized and evaluated as lubricant additives in MACs for steel/steel contact. The ILs were simply prepared by blending an appropriate molar ratio of C<sub>3</sub>N<sub>3</sub>(OR)<sub>3</sub> or P<sub>3</sub>N<sub>3</sub>(OR)<sub>6</sub> and LiTFSI together. The friction and wear test results showed that these ILs have excellent friction-reducing, anti-wear and high load-carrying properties that are far better than those of the commonly used lubricant additive T204. These ILs can be regarded as a new type of multifunctional lubricant additive for MACs that can satisfy the requirements of modern technology. Further studies of other lithium-based and functionalized ILs, such as ILs with anti-corrosion groups, as lubricant additives for MACs are underway in our laboratory.

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