"Exemption Application from PFAS Restrictions for Ionic Liquids"

I. About LANDE

Zhejiang Lande Energy Technology Development Co., Ltd. (referred to as Lande Technology) was established in 2009, with a registered capital of USD 4.695 million and total assets of USD 30.14 million. The company was recognized as a provincial-level R&D center in 2021 and a specialized, refined, and innovative enterprise in Zhejiang Province in 2022.

As a representative enterprise in the field of ionic liquid new materials, Lande Technology, as one of the key listed enterprises cultivated by the Zhejiang Provincial Government's "2025 Phoenix Plan", is a leading enterprise in the segmented field of ionic liquid new materials. The company has completed angel, A-series, and B-series equity financing, and is currently valued at USD 68.5 million. In the next three years, the company will complete the strategic layout of setting up two production bases and two enterprise research institutes in the Guangdong Hong Kong Macao Greater Bay Area and the Yangtze River Delta Greater Bay Area as soon as possible through the power of capital. It will conduct research on the application of ionic liquid new materials in various fields, expand new and old markets through technological innovation, and strive to complete the IPO work of the A-share capital market in the first three years of 2025.

II. About Ionic Liquids

Ionic liquids (ILs), also known as "molten salts", are salts composed of organic cations and inorganic anions that are in a liquid state below 100 °C. They are non-volatile, non-flammable, highly conductive, and have a high viscosity at room temperature (usually 1-3 orders of magnitude higher than traditional organic solvents. The interaction between van der Waals forces and hydrogen bonds inside ionic liquids determines their viscosity), high heat capacity, low vapor pressure, and stable properties, it has good solubility for many inorganic salts and organic compounds and is widely used in fields such as electrochemistry, organic synthesis, catalysis, separation, etc. It is a good substitute for traditional organic solvents. Due to the diversity of organic cations and inorganic anions, by changing the ratio combination, different ionic liquid new materials with special functions can be designed and synthesized according to different usage conditions [1].

Here’s an overview of ionic liquids:

Chemical Structure:

Ionic liquids are usually composed of a combination of cations and anions. Most PFASs are covalent compounds.

Characteristics:

Ionic liquids typically remain in a liquid state at room temperature and exhibit high thermal stability. They are non-volatile and have high boiling points, making them suitable for use under high vacuum or high-temperature conditions. They often possess excellent electrical conductivity, solubility, and chemical stability, making these properties valuable in various industrial fields.

Applications:

Ionic liquids find wide applications in various industries, including organic synthesis chemistry, catalysis, electrode materials, electrolytes, energy storage technologies, metal refining, gas absorption, green chemistry, analytical chemistry, and biological research, among others. Notably, they play a crucial role in the development of sustainable chemical processes and energy conversion technologies, such as battery electrolytes for electric vehicles (EVs), at the same time, it has also received attention as a substitute for some existing PFASs.

Environmental Impact:

At present, research generally believes that ionic liquids are green and safe, not only can they be used for recycling and treating waste in various industries, but also easy to recycle and reuse, which is of great significance for environmental protection [2] ~ [4].

Research and Development:

Research and development related to ionic liquids are advancing steadily, the characteristic of its' customizable structure 'implies infinite potential. It will bring new development prospects to many fields. Ionic liquids are drawing attention in fields such as chemistry, energy, the environment, and materials science due to their diverse properties and applications. Their potential value as a sustainable technology is highly regarded [4].

III. PFAS-Relevant Substances in Ionic Liquids on EU issue

Traditional long chain perfluoroalkyl and multifluoroalkyl compounds are a type of organic compounds with alkyl chains as the backbone and hydrogen atoms partially or completely replaced by fluorine atoms. They have the characteristics of low surface tension, low viscosity, hydrophobicity, and oil repellency. It is widely used in textile dyeing, coatings, leather, cooking utensils, food packaging, synthetic detergents, insecticides, and other fields, as well as in chemical, firefighting, construction, machinery, and aerospace. PFASs are difficult to degrade and easy to accumulate in the natural environment, and have significant toxic effects on almost all biological growth and development. Studies have shown that the degradation rate of PFASs in organisms is not only related to species and gender, but also to carbon chain length [5] ~ [7].

According to the EU PFAS restriction proposal, bis(trifluoromethylsulfonyl)imides (TFSI) in Lande's ionic liquid products are also recognized as one of the PFASs subject to restrictions. In fact, TFSI is one of the most commonly used anions in the ionic liquid industry when designing molecular structures. The following are the TFSI anion product numbers, English names, and CAS numbers for Lande:

LDAM-102: Tributylmethylammonium bis(trifluoromethylsulfonyl)imide CAS NO. 405514-94-5

LDIM-212: 1-Ethyl-3-Methylimidazolium bis(trifluoromethylsulfonyl)imide CAS NO. 174899-82-2

BMPTFSI: N-methyl, butyl pyrrolidinium bis(trifluoromethylsulfonyl)imide CAS NO. 223437-11-4

PP14TFSI: N-methyl, butylpiperidinium bis(trifluoromethylsulfonyl)imide CAS NO. 623580-02-9

LDPY405: (N-butylpyridinium bis(trifluoromethylsulfonyl)imide) CAS NO. 187863-42-9

LDPR423: (N-(2-Methoxyethyl)-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide) CAS NO. 757240-24-7

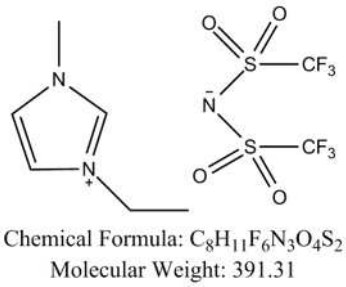

Fig. 1 1-Ethyl-3-Methylimidazolium bis(trifluoromethylsulfonyl)imide structural formula (TFSI anion on the right)

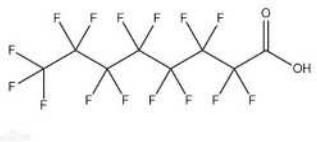

Fig. 2 Structural formula of perfluorooctanoic acid (PFOA)

Fig. 1 shows the structural formula of LDIM-212:1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides salt, which is the most commonly used TFSI anion salt. Fig. 2 shows the structural formula of perfluorooctanoic acid (PFOA) in traditional long-chain PFASs. It was certified as a suspected human carcinogen by the International Institute of Cancer Research (IARC) in 2014. The fluorine content of LDIM-212 is 29%, and the fluorine content of perfluorooctanoic acid is 68%, which is a significant difference between the two. It is not difficult to see that there is a significant difference in the structure between the two. Currently, toxicological research on PFASs suggests that their toxicity to organisms is closely related to their structural susceptibility to binding

to human blood albumin [8].

Therefore, it is inaccurate to assume that both TFSI ionic liquids and traditional long-chain fluorinated compounds have toxic effects on organisms solely based on their -CF_3 properties.

At the same time, TFSI ionic liquids have different uses from traditional long-chain fluorinated compounds. In TFSI ionic liquids, the anions and cations are weakly coordinated, and TFSI is also a very good electrophilic and nucleophilic leaving group. It is mainly used for catalyzing various chemical reactions. Lithium salt of TFSI is also one of the most excellent lithium battery electrolytes at present. Ionic liquids, unlike PFASs, are not widely used in various situations, which also means that it is difficult to affect the ecology on a large scale like PFASs. Ionic liquid catalysts and ionic liquid electrolyte batteries are also easier to control in practical industrial production.

IV. Safety of TFSI anion

EU is considering “one-size-fits-all” regulations for PFAS. However, there hasn't been sufficient research conducted on the potential harm of TFSI anions. For instance, while PFAS are a cause for concern due to their potential for long-term accumulation in the body and carcinogenic effects, as far as our research indicates, there haven't been experimental findings suggesting such harm from TFSI anions. As an example, there are reviews stating that no studies have confirmed the carcinogenicity of the most well-known TFSI salt, LiTFSI [9].

In light of this situation, it is believed that applying “one-size-fits-all” regulations to ionic liquids containing TFSI may be premature due to insufficient information [10].

V. Alternative substances for TFSI anion

Regarding the primary application of ionic liquids containing TFSI anions, which is as electrolyte additives for electric vehicles (Evs), research and development have been ongoing at research institutions worldwide since around 2000. However, as of September 2023, to the best of our knowledge, no alternative substances have been announced.

VI. The social and economic losses & impacts resulting from the restriction of ionic liquids (with PFAS anions)

The primary application, electric vehicles (Evs), represents an indispensable and crucial market for mitigating global warming and reducing CO_2 emissions. Ionic liquids (with PFAS anions) play a significant role in enhancing the safety of Evs as electrolyte additives [11], [12].

The importance of safety in electric vehicles (Evs) can be explained as follows:

High-Voltage Batteries: Evs utilize high-voltage lithium-ion batteries. These batteries are highly efficient and have a high energy density. However, this high voltage and stored energy pose increased risks in the event of accidents or failures. Therefore, the design, manufacturing, handling, and protection of these batteries are of utmost importance.

Fire Risk: EV battery packs can potentially ignite when exposed to high temperatures, presenting a fire risk. In the event of battery damage or accidents, fires can jeopardize the safety of occupants. Consequently, battery pack designs must incorporate measures to mitigate fire risks.
Several research papers have discussed how ionic liquids can address these issues effectively in Evs [13] ~ [15].

The global market for ionic liquids is expected to grow to 65,000 metric tons per year by 2024, reaching a market size of USD 2.5 billion. In order to solve energy problems in the future, new energy batteries will not only be used in electric vehicles, but also cannot achieve the best of both economic and environmental benefits if ionic liquids are restricted [16].

VII. Conclusion

In summary, in the face of the EU's restriction proposal, it is lack of scientific and reasonable to restrict Lande ionic liquid products in terms of their impact on the environment; Restricting the use of Lande ionic liquid products is not conducive to the development of new energy and industry. Therefore, we request a review and revision of PFAS restrictions to exclude Lande ionic liquid products from such regulations.

VIII. Reference:

[1] https://chemicals.basf.com/global/en/Intermediates/Product_groups/Ionic_liquids.html
[2] https://www.sciencedirect.com/science/article/abs/pii/S1381116901004654
[3] https://www.nstl.gov.cn/paper_detail.html?id=180735077240f9944cfbfb7987d9a7e0
[4] https://www.researchgate.net/publication/242484306_A_short_history_of_ionic_liquids_-_From_molten_salts_to_neoteric_solvents
[5] https://pubmed.ncbi.nlm.nih.gov/11311214/
[6] https://www.researchgate.net/publication/23469652_Modeling_Single_and_Repeated_Dose_Pharmacokinetics_of_PFOA_in_Mice
[7] https://www.nstl.gov.cn/paper_detail.html?id=16d8b28bc531ca534686377afa25c8dd

[8] https://www.zhangqiaokeyan.com/journal-foreign-detail/0704029054205.html
[9] https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=358288&Lab=CPHEA
[10] https://pubs.acs.org/doi/10.1021/acs.chemrev.7b00246
[11] https://www.fortunebusinessinsights.com/industry-reports/electric-vehicle-market-101678
[12] https://www.iea.org/news/global-electric-car-sales-have-continued-their-strong-growth-in-2022-after-breaking-records-last-year
[13] https://www.sciencedirect.com/science/article/abs/pii/S2589778022000070
[14] https://pubs.rsc.org/en/content/articlelanding/2021/ee/d0ee04002a
[15] https://www.researchgate.net/publication/340713918_Ionic_Liquid-Based_Electrolytes_for_Energy_Storage_Devices_A_Brief_Review_on_Their_Limits_and_Applications
[16] https://zhuanlan.zhihu.com/p/652672090