HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

TANDEM FOREST VALUES
Sweden's gift to Finland 2017

KTH VETENSKAP OCH KONST

0. General descriptors of the project:

Name: *"Fusion wood"*

Principal Investigator: **Prof. Paula Eerola,** Faculty of Science

Project Leader: **Prof. Ilkka Kilpeläinen,** Department of Chemistry (HY), ilkka.kilpelainen@helsinki.fi, +35850 5181148

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1. Initial aim:

This consortium project aims to synergistically combine the solid expertise of both partners towards the creation of a multidisciplinary research platform able to provide novel far-reaching contributions in the lignocellulosic biopolymeric scientific and technological field. To this end, **our approach involves the design, production, characterization and investigation of the properties of novel ionic liquid based on phosphorous-containing novel groups**.

Why Ionic Liquids?

Ionic liquids are molten salts containing one or more cations that have privileged properties for their use as solvents such as: (i) Low vapour pressure and flammability, (ii) great versatility in their structural design and thus their properties, (iii) unique ability to engage and foster intermolecular interactions such as hydrogen bonding and/or stabilization of elusive ionic species, (iv) relatively low toxicity in comparison to many organic solvents, (v) amenability for recycling, (vi) chemical stability, (vii) intrinsic conductivity.

In the last years, the Kilpeläinen group has enjoyed a leading role on the investigation and application of such ionic liquids as solvents in chemical processes to process and impart new properties to lignocellulosic materials. **This is a highly promising approach in the lignocellulosic field** where the poor solubility and relative inertness of the starting biopolymers often hampers their chemical and/-or technological modification, thus obstructing the valorization of these materials through novel applications. **Additionally**, ionic liquid have shown an extraordinary potential to reduce the crystallinity, control the particle size and topology of lignocellulosic biopolymers *a-la-charte*.

Why Phosphorous-based Ionic Liquids?

Phosphorous is a highly oxyphilic element with unparalleled diversity in the structure and properties of its compounds. In the biopolymer area, phosphorous compounds have attracted considerable interest due its ability to impart anti-flammable properties. **Our hypothesis was that the potential of some phosphorous oxygenated compounds to engage in intermolecular interactions such as the ones involved in the dissolution and chemical modification of lignocellulosic materials, could be coupled to the distinctive advantages inherent to superbasic amidine and/or guanidine-based cations broadly used in our group.**

As such, we developed unprecedented ionic liquids whose properties and potential, we would then explore in tandem with the research group of Prof. Berglund.

2. Chronology of the project (up to date)

The polyhedral nature of the research aimed in this project demanded the hiring of a PhD-qualified chemist with a broad range of synthetic skills, experience in phosphorous chemistry, and demonstrated ability to participate in multidisciplinary projects both conceptually and experimentally. We devised that only on this manner we could design and develop our targeted phosphorous-based ionic liquids. As such, we selected Dr. Jesus Perea-Buceta (University Researcher, Academy of Finland Research Project consortium co-PI, doctoral expertise in total syntheses of organic molecules, postdoctoral experience on coordination chemistry, homo- and hetero-geneous catalysis, as well as medicinal chemistry) as the most competent candidate for this role during the duration of the project (1st June 2019-31st March 2021).

June-September 2019: Dr. Perea-Buceta and Prof. Kilpeläinen conceived the initial masterlines of the project considering the existing literature and the research ongoing at both research groups.

September-November 2019: Dr. Perea-Buceta designed, purchased the required starting materials, and conducted the synthesis of candidate phosphorous-containing ionic liquids. Special attention was placed to consider alternate plan and/-or research lines to contend any unforeseen setback that could arise.

22th November 2019: Prof. Berglund visited the University of Helsinki and discussed with Dr. Perea-Buceta and Prof. Kilpeläinen the implementation of the designed plan of action in the context of Prof. Berglund research. **A three-days research visit during January to KTH Stockholm** was agreed for Dr. Perea-Buceta to get acquainted with the research and group of Prof. Berglund.

December 2019- January 2020: Dr. Perea-Buceta conducted the initial large multi-gram scale syntheses of several phosphorous-based ionic liquid candidates that later would be investigated at KTH.

***31st January-2nd February* 2020:** Dr. Perea-Buceta visited for three days the Wood Science Center at KTH where Prof. Berglund is based. The details, materials, and personnel required to participate in the project were thoroughly discussed.

It was agreed that:

- From the KTH side of the consortium Assoc. Prof. Li would join in a primary role to co-supervise the research and assist in the research implementation. PhD candidate Jonas Garemark also manifested his will to investigate the properties of the novel phosphorous-based ionic liquids in the context of his research.

- From the HY side of the project, PhD candidate, Rico del Cerro, would assist Dr. Perea-Buceta in the initial exploration of the properties of the ionic liquids on lignocellulosic models.

- Three distinct lines of research based on the utilization of phosphorous ionic liquids were established:

  - The investigation of ionic liquids for the dissolution of cellulose and/-or production of novel aerogel porous materials (PhD candidate Jonas Garemark, Assoc. Prof. Yuanyuan Li).

  - The investigation of hybrid cellulosic-MoS2 bio-composites with potential novel optoelectronic properties and as nanomaterials (Dr. Perea-Buceta- Assoc. Prof. Yuanyuan Li)

  - The investigation of hybrid cellulosic-molecular magnets bio-composites (Dr. Perea-Buceta- Assoc. Prof. Yuanyuan Li).

February 2020: Dr. Perea-Buceta assisted by PhD candidate, Rico del Cerro prepared all the materials to be delivered at KTH. The preliminary studies on three lines of research was also carried out.

***1st-3rd March* 2020:** Dr. Perea-Buceta and PhD candidate, Rico del Cerro visited for three days the Wood Science Center at KTH. The agreed phosphorous ionic liquids were delivered. Dr. Perea-Buceta and Rico del Cerro instructed Dr. Li and PhD candidate Garemark on the handling, manipulation and basic properties of ionic liquids. It was also agreed and arranged by Dr. Li an extended visit for Dr. Perea-Buceta at KTH during May and June 2020. This period would enable Dr. Perea-Buceta to gain further insight on the research carried out at KTH and conduct hand-in-hand with Dr. Li the research lines agreed on January.

March-August 2020: The unfortunate global outbreak of the COVID-19 pandemic directly prevented Dr. Perea-Buceta to proceed according to the plan and visiting KTH in summer 2020. The health authorities of Finland and the University of Helsinki strictly recommend to avoid visits to countries with more of 10 cases per 100,000 habitants such is Sweden. In the current context is difficult to anticipate how the situation will evolve in the next months, and if it would be possible to resume research visits between HY and KTH during winter 2020-2021.

September 2020-April 2021 (End of project) The researcher exchange between University of Helsinki and KTH could not be carried out as planned. This was due to the unfortunate situation with COVID-19 pandemia and the national and University of Helsinki regulations. Therefore, also the budgeted funding for travelling remained essentially unused. To make the best despite the current (still continuing) conditions, the researchers organized regular video meetings and other direct communication. Foremost, the exchange of data and materials was actively pursued through international carriers and postal service

3. Major results of the project

As expected, the developed novel phosphonium ionic liquids turned were not efficient solvents for cellulose. However, it was originally expected that they would swell cellulose fibers and would thus provide a controllable pathway towards 'chemical welding' of cellulose and wood. In this, the IL's only performed moderately and it was not possible to find proper processing/treatment conditions for high performance.

To our surprise, two of the novel phosphonium ILs ([MTBD][MMP] and [MTBN][MMP]) were opening wood cellular structure 'inside' the pores, as shown in Figure 1. This allowed turning delignified wood directly to nanoporous aerogels – a phenomenon that has never been observed earlier.

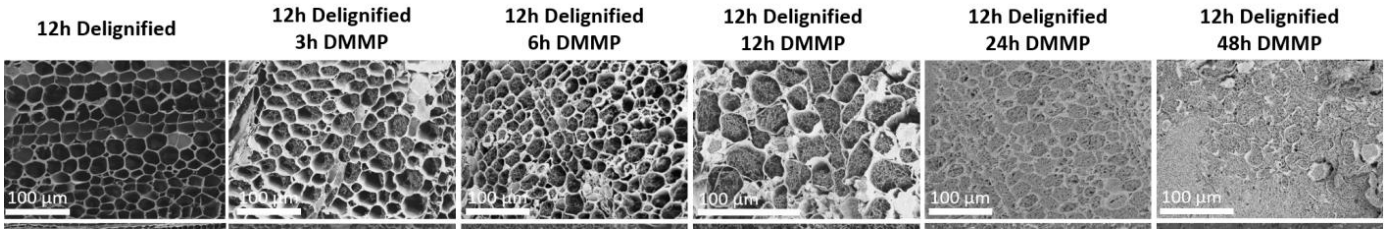

Figure 1. The treatment of delignified wood with a novel phospjonium IL. Th ephosphonium IL fibrillates the pores of wood 'inwards', but does not detach the cells from each other. The physical outlook of the preated wood remains essentially intact, but the pores turn to 'aerogels'. Courtesy of Jonas Garemark, KTH

The effect of the IL seems to relate to a constant dissolution-regeneration process of cellulose. Thus, eventhough these ionic liquids are not able to macroscopically dissolve cellulose, the allow the cellulose network to re-organize to a new organized structure/network.

The mechanical properties of these novel wood aerogels are considerably better than earlier aerogels formed from a dissolution/regeneration process of cellulose. Further, the removal and recovery of the ionic liquid is straightforward with simple washing.

These findings offer a simple and efficient route to wood-base aerogels for different applications (light-weight materials, composites, absorbent sponges or slow-release matrixes), but their applicability is still to be demonstrated. We are currently working with three manuscripts on this topic: i) synthesis of these ILs and their properties, ii) swelling of wood/formation of wood aerogels and iii) phenomena leading to this unexpected behavior.

4. Expenditure of the funds

The funds were used for post-doc (Jesus Perea) salaries and directly related reagent (chemicals) and small laboratory commodity costs (see separate report from UH administration). due to the COVID-19 pandemia, the planned researcher visits could not be carried out as planned and that part of the budget remained mainly unused-

Helsinki 30.6.2021

Ilkka Kilpeläinen