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The effect of ionic liquids on germination and physiological traits of wheat and barley

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Ionic liquids (Ils)...

- An intensive research in the field of green chemistry is devoted to design environmentally friendly (green) solvents.
- One of the most popular strategies is synthesis of new classes of ionic liquids (Ils).
- Ils are innovative solvents of 21st century with a wide range of potential applications.
- Ils are mostly salts made of organic/inorganic ions which are liquid at room t° .
- Many Ils are synthesized from organic cations: **imidazolium**, pyridinium, phosphonium etc...
- Many Ils are commercially available.

Properties of IIs...

- Negligible vapor pressure
- Good thermal stability
- Nonflammability
- Wide electrochemical window
- Good extraction capability
- Low volatility (atmospheric pollution is unlikely)



- IIs are heterogeneous group of liquids which **cannot be considered a priori benign.**

Environmental application of IIs...

1. **Enrichment of environmental pollutants:** IL-based sample methods have been applied for extraction of organic analytes like substitute benzene derivates, biofuels, PAHs, pesticides, bactericides etc.
2. **Removal of environmental polutants:** heavy metal pollution, biotreatment of uranium, removal of boron chromate from the water, removal of organic contaminants from the soils, extraction of DDT, dieldrin and hexachlorobenzene...
 - However, some IIs **may contaminate** soils, sediments, surface and groundwater. Therefore, it is essential to have comprehensive understanding of their properties.
 - **Toxicity of IIs** depends on their interaction with cellular membranes, which mainly depends on IL type (**alkyl chain lenght, cation family and anion**).

Imidazolium based IIs...

In our study, 5 different imidazolium based IIs were synthesised and their toxicity towards wheat and barley was investigated:

1. 1-(2-oxybutyl)-3-methylimidazolium chloride ($[C_2OC_2mIm][Cl]$)
2. 1-(2-oxypropyl)-3-methylimidazolium chloride ($[C_1OC_2mIm][Cl]$)
3. 1-(3-hydroxypropyl)-3-ethylimidazolium chloride ($[C_3OHeIm][Cl]$)
4. 1-(3-hydroxypropyl)-3-methylimidazolium chloride ($[C_3OHmIm][Cl]$)
5. 1-(2-hydroxyethyl)-3-methylimidazolium chloride ($[C_2OHmIm][Cl]$)

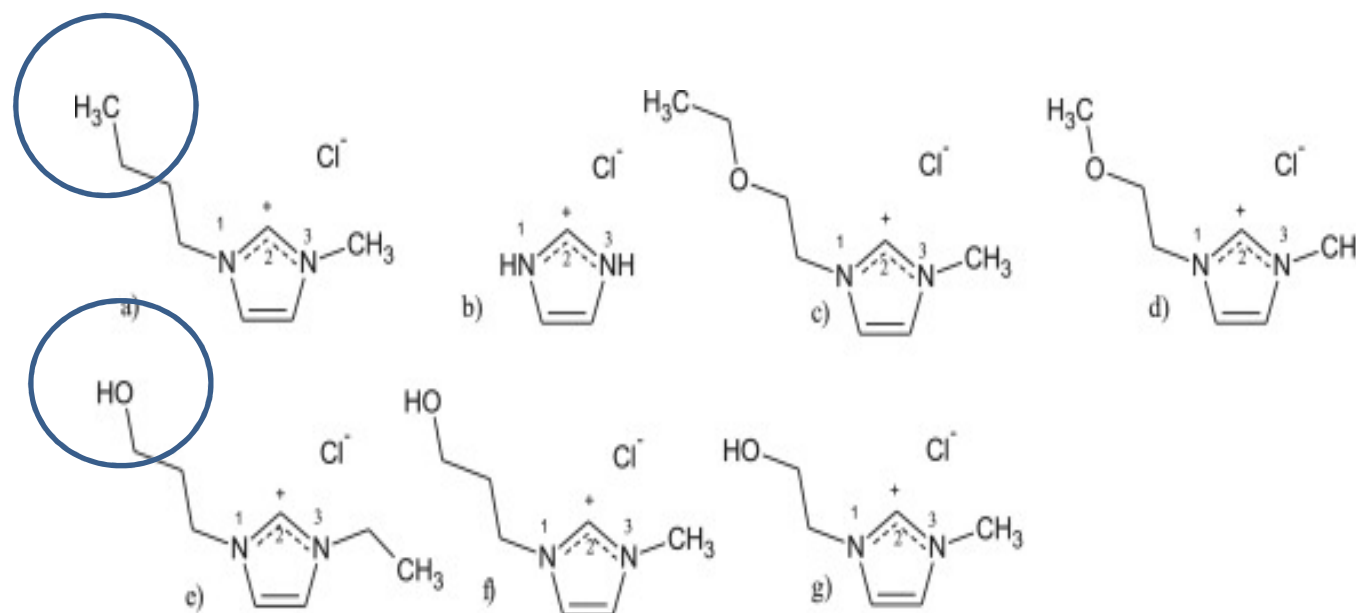
...and two commercial IIs

1. 1-butyl-3-methylimidazolium chloride ($[BmIm][Cl]$)
2. protic imidazolium chloride ($[Im][Cl]$)

Structure of investigated IIs

- a) [BmIm][Cl]
- b) [Im][Cl]
- c) [C₂OC₂mIm][Cl]
- d) [C₁OC₂mIm][Cl]
- e) [C₃OHelm][Cl]
- f) [C₃OHmIm][Cl]
- g) [C₂OHmIm][Cl]

*These compounds are room temperature IIs with one side chain functionalized with oxygen in form of **hydroxyl** or **ether** group except **protic imidazolium salt and [BmIm][Cl]**.



Material and methods...

- Seeds of **wheat** and **barley** were sown in glass Petri dishes to which 7.5 mL of either deionized water (control) or 10, 100 or 1000 mg/L of selected II was added.
- Germination was done at 26 °C.
- Number of germinated seeds was counted after **24, 48** and **72 h** (120 h from sowing).
- 8 seedlings from each Petri dish was transfered to pots filled with 750 mL of $\frac{1}{2}$ **Hoagland solution**.
- Plants were grown in growth chamber under controlled conditions.
- After 8 days, plants were harvested and the following parameters were assessed: **root and shoot lengths (cm), dry weight (g), % of growth inhibition**.
- Experimental data were analyzed with **Origin 8.1** statistical software, by one-way ANOVA.
- All of selected IIs were synthetized or purchased on **Departement of Chemistry** (Faculty of Sciences).

Results...

Effects on germination of wheat

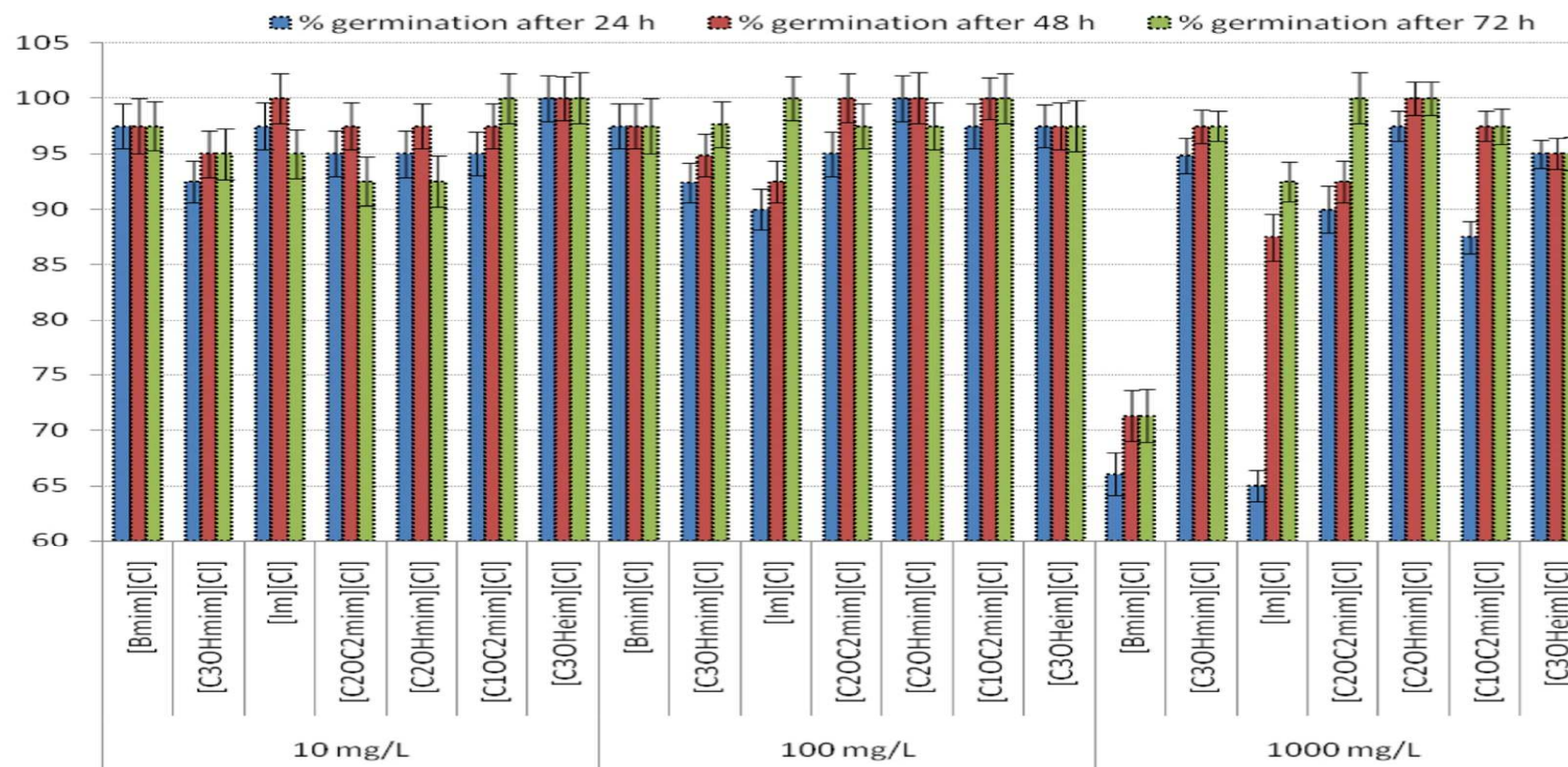


Fig 1. Effects of investigated IIs and salts on germination of wheat at every applied concentration (10, 100 and 1000 mg/L)

Results...

Effects on germination of wheat

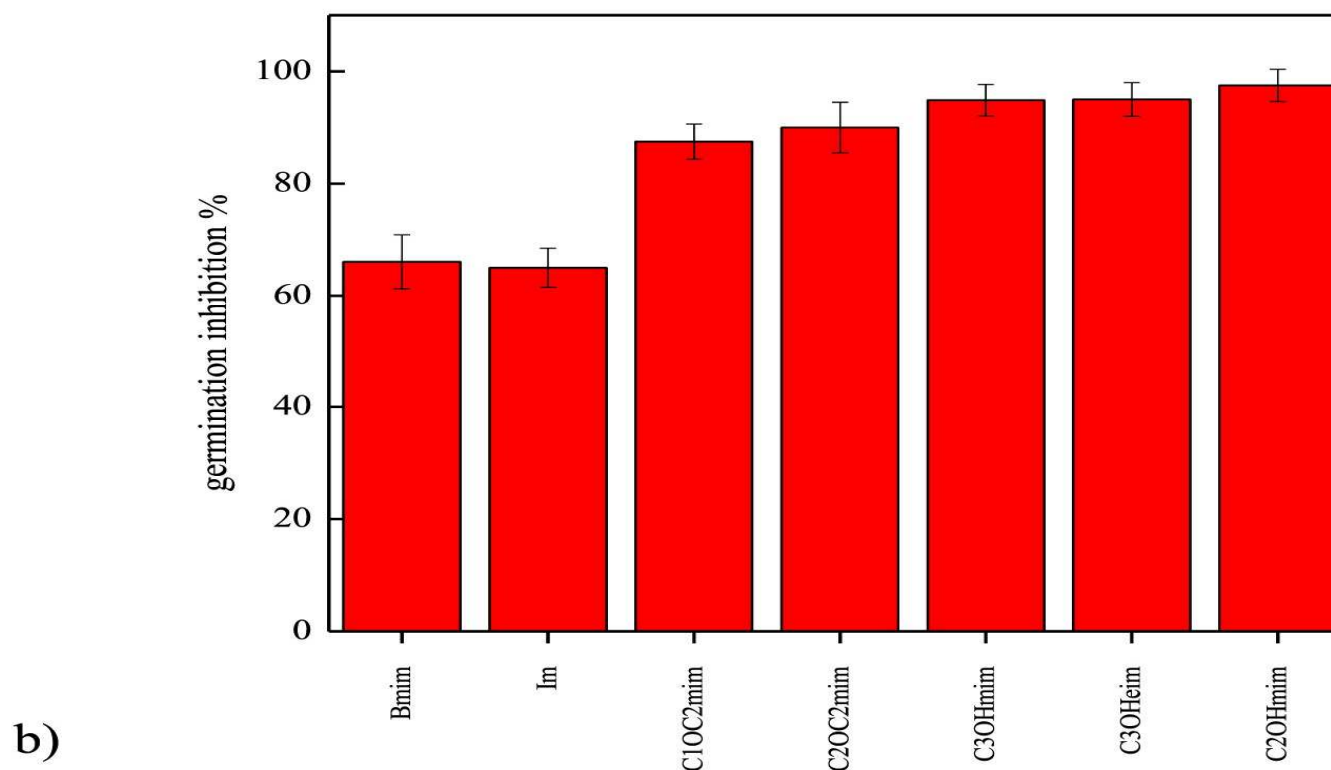


Fig 2. Effect of investigated IIs and salts on germination of wheat at the highest concentration of 1000 mg/L

Results...

Effects on germination of barley

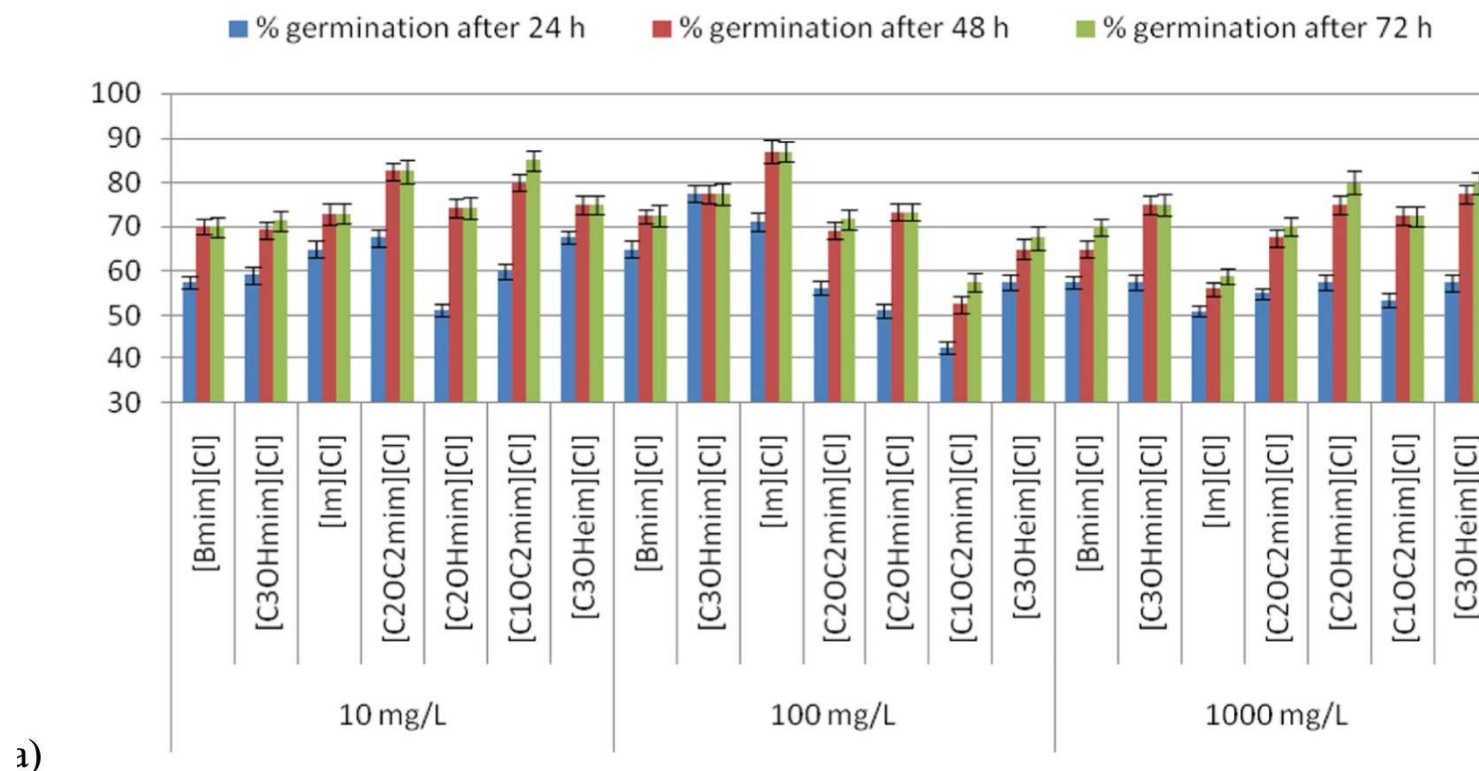


Fig. 3. Effects of investigated IIs and salts on germination of **barley** at every applied concentration (**10, 100 and 1000 mg/L**)

Results...

Effects on germination of barley

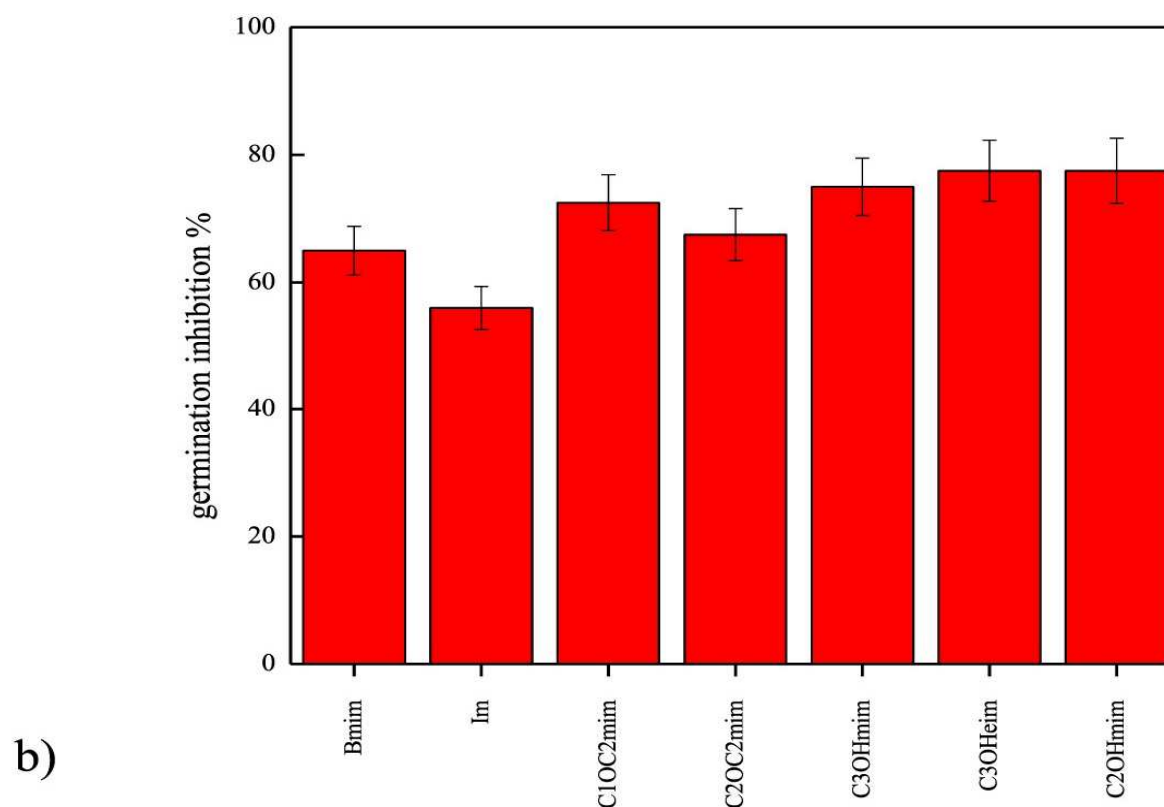


Fig. 4. Effect of investigated IIs and salts on germination of **barley** at the highest concentration of **1000 mg/L**

Results...

Effects on growth of wheat and barley

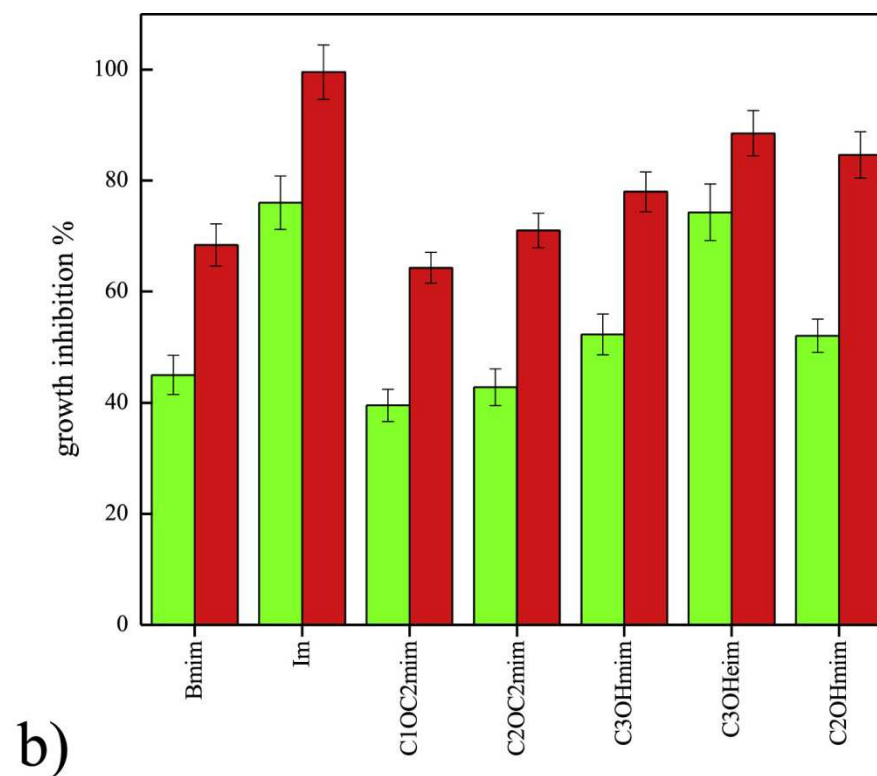
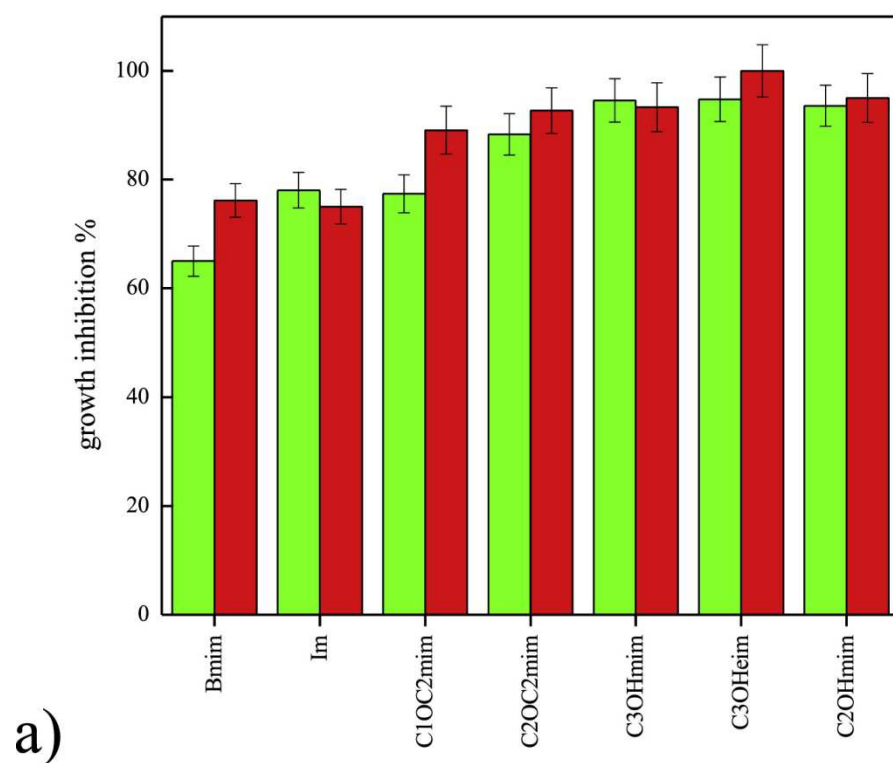
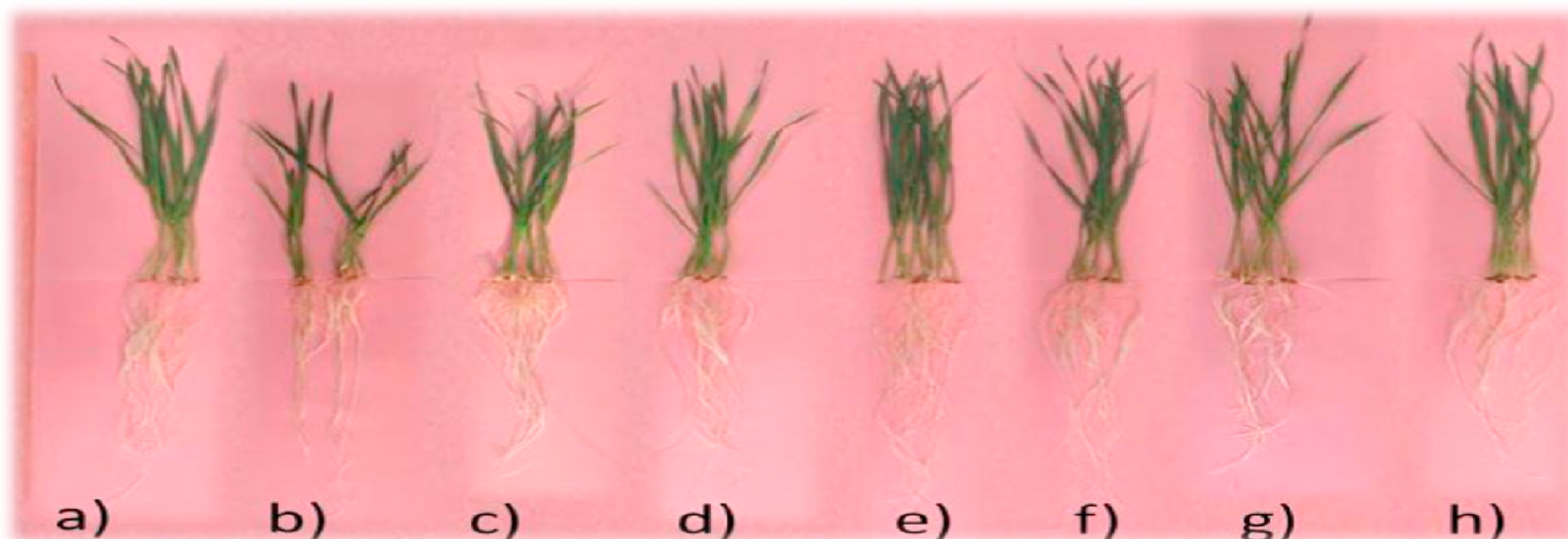


Fig. 5. Effects of IIs on growth of a) **wheat** and b) **barley** seedlings (green- **root**, red **shoot**)

Results...

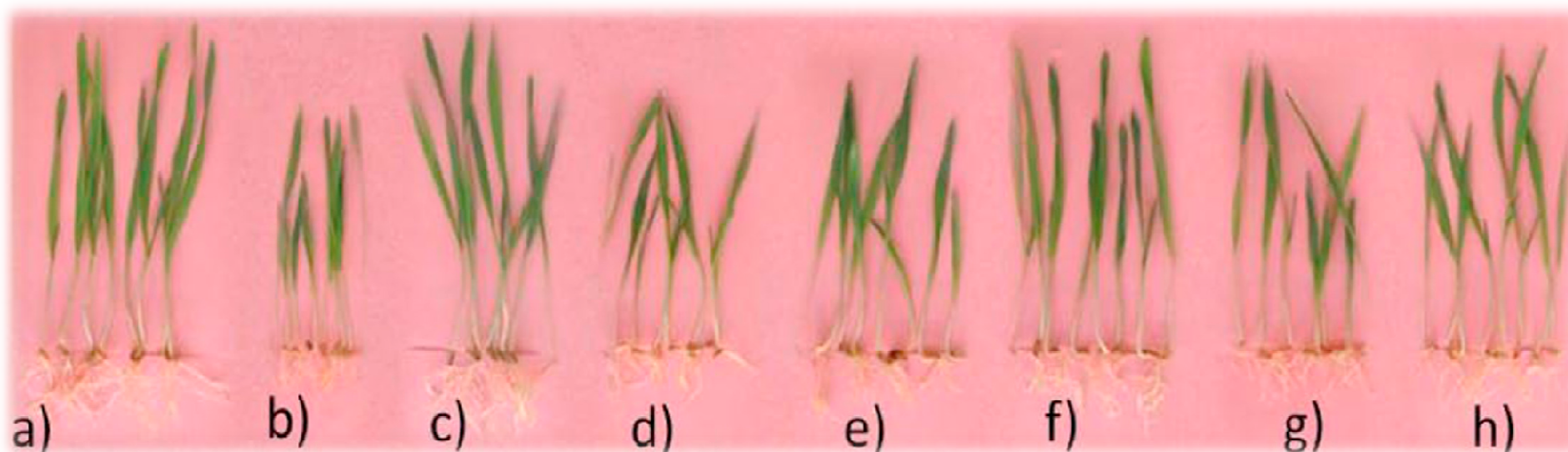
Effects on growth of wheat



Wheat seedlings after treatment with different IIs (1000 mg/L). a) control b) $[BmIm][Cl]$ c) $[Im][Cl]$ d) $[C_2OC_2mIm][Cl]$ e) $[C_1OC_2mIm][Cl]$ f) $[C_3OHeIm][Cl]$ g) $[C_3OHmIm][Cl]$ h) $[C_2OHmIm][Cl]$

Results...

Effects on growth of barley



Barley seedlings after treatment with different IIs (1000 mg/L). a) control b) [BmIm][Cl] c) [Im][Cl] d) [C₂OC₂mIm][Cl] e) [C₁OC₂mIm][Cl] f) [C₃OHmIm][Cl] g) [C₃OHmIm][Cl] h) [C₂OHmIm][Cl]

Conclusion...

- The objective was to investigate the influence of length and oxygen functionalization on toxicity of imidazolium based IIs towards wheat and barley.
- **Germination and growth** of barley and wheat did not respond equally to the presence of IIs.
- Even though they both belong to **Gramineae**, there is species specific response with respect to interactions between IIs and cell membranes and their overall effect on growth.
- **Oxygen functionalization** of side chain **reduced** toxicity of IIs (introduction of **hydroxyl** group).
- **Additional prolongation of alkyl chain** reduces toxicity even more,
- The collected results on the IIs effect on germination and growth of small grains may be useful for assessing the potential risk to humans, as well as guidelines to design new non-toxic IIs, by variation of their lipophilicity.



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The effect of imidazolium based ionic liquids on wheat and barley germination and growth: Influence of length and oxygen functionalization of alkyl side chain



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Thank You all for your attention!