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IONIC LIQUID
LABORATORIES

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Structure-property relationships in new LCST ionic liquids

Sanskrita Madhukailya

Confidential, QUILL Meet 25th-26th March 2024

Lower Critical Solubility Temperature (LCST)

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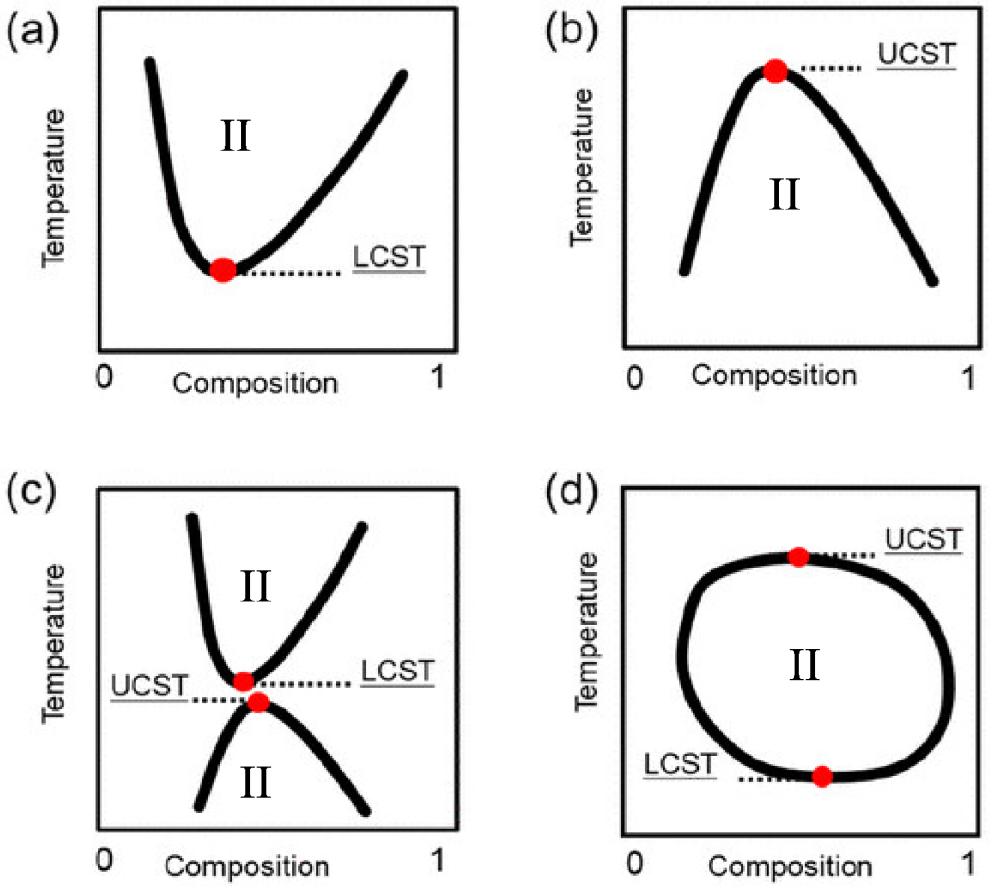

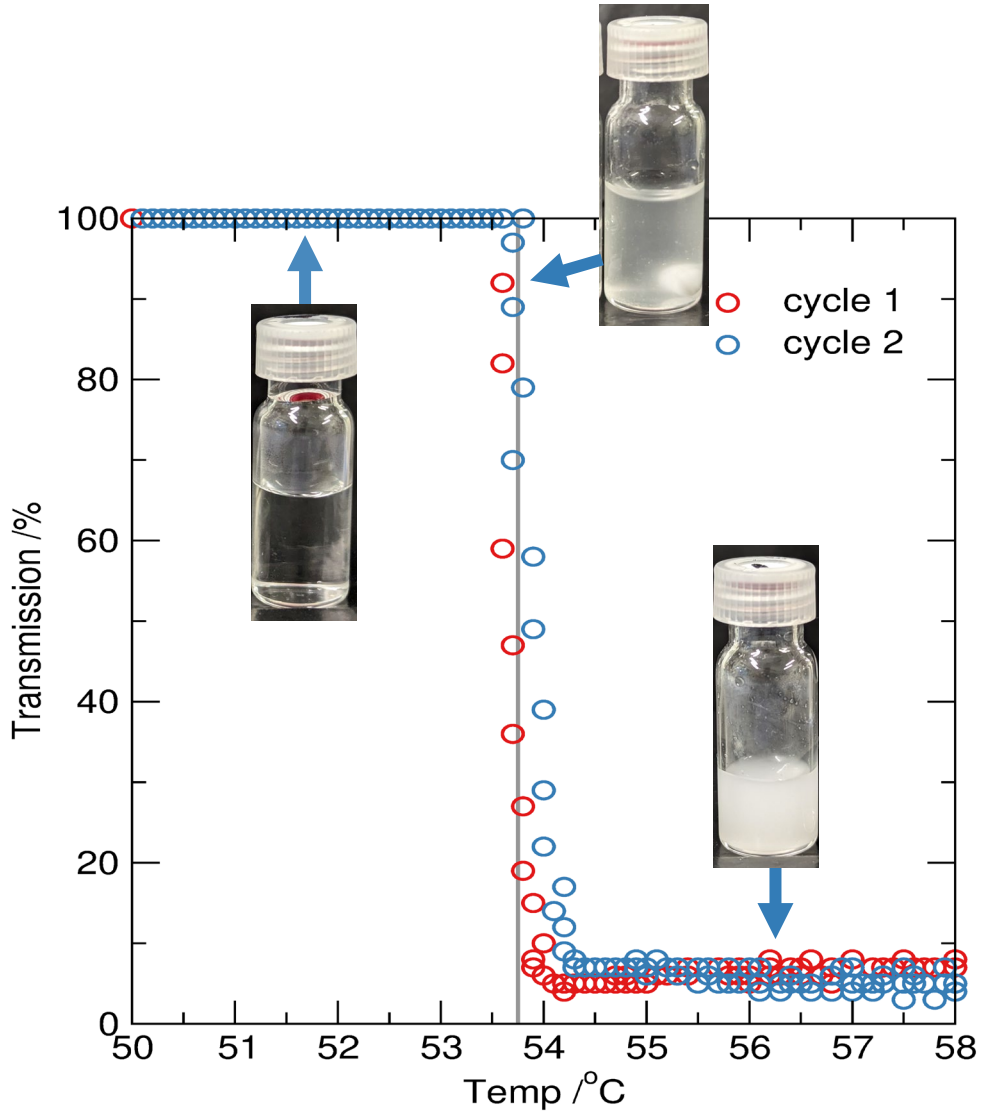

Ballone et. al., *Molecules* **2022**, *27*(5), 1647

LCST over the years..

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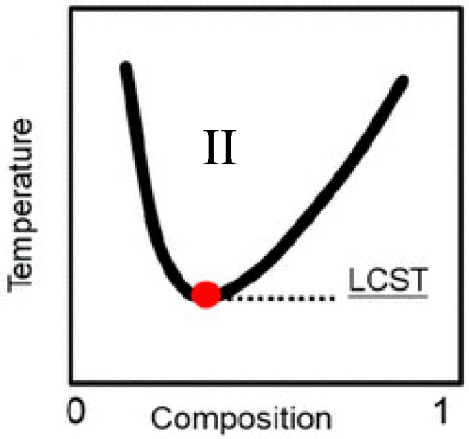
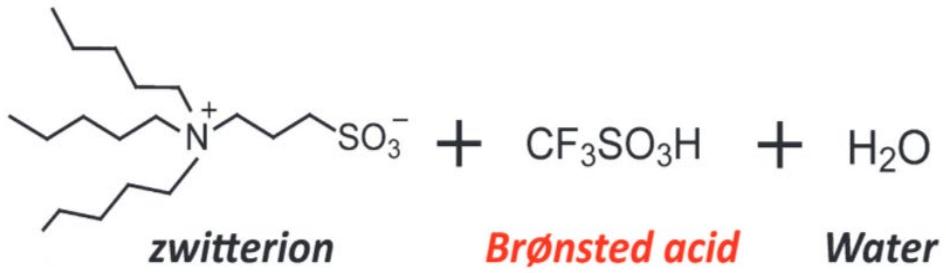
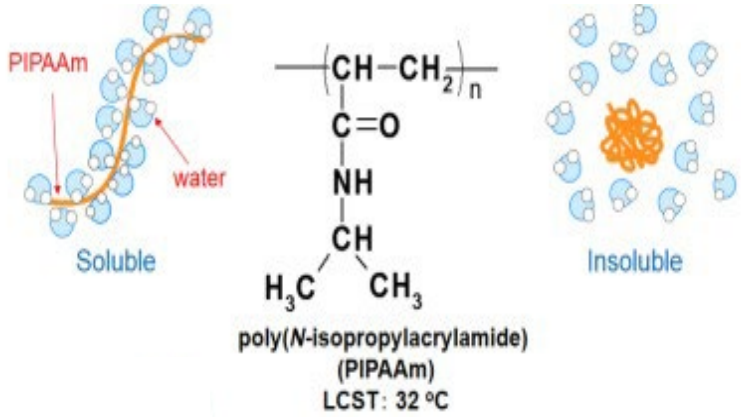






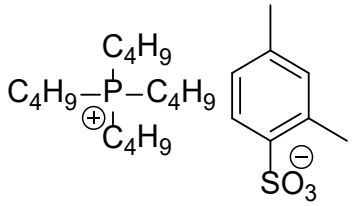
Cellulose Derivatives (1930s)

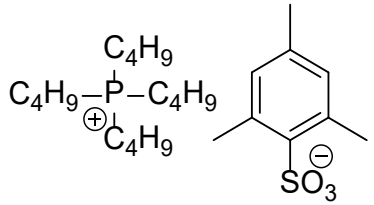
Polymers (late 1950s)

Ionic Liquids (2007)

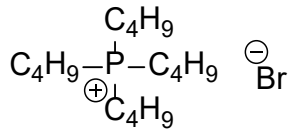
Zwitterionic Ionic Liquids (2016)

sulfonates

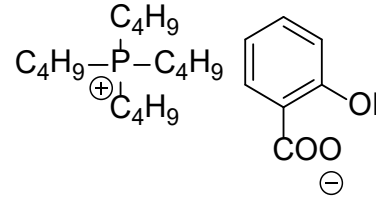




halides



carboxylates



Heskins et. al., *J. Macromol. Sci.*, **1968**; Ohno et. al., *Angew Chem.*, **2007**: 1852-1855.; Ohno et. al., *Chem.Eur.J.* **2016**,22,12262–12265

LCST over the years..

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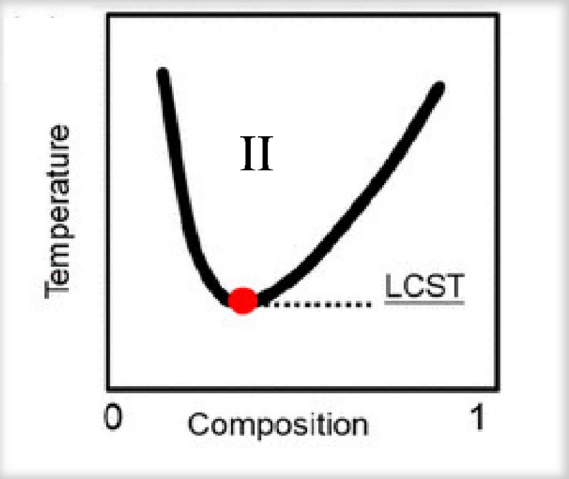
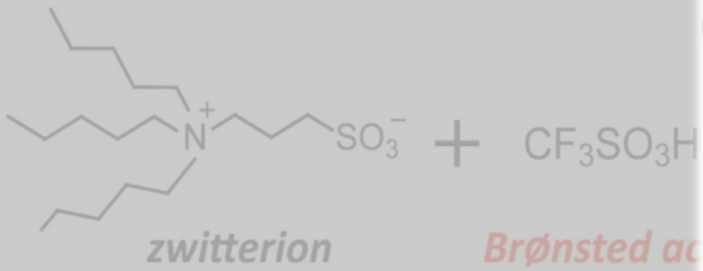




Communications

Ionic Liquids

DOI: 10.1002/anie.200604402

LCST-Type Phase Changes of a Mixture of Water and Ionic Liquids Derived from Amino Acids**

*Kenta Fukumoto and Hiroyuki Ohno**

Ionic liquids (ILs)[1] are organic salts designed to melt below 100°C, in particular at room temperature, which have characteristic properties such as negligible volatility[2] and nonflammability over a wide temperature range. There is increasing interest in ILs that have functional groups designed

diagram reported was only observed at high and limited IL content (60–65%). There was no direct demonstration of clear phase separation above the critical temperature. It is desirable to arrange similar LCST-type phase separation in water/IL mixtures, because the partition coefficient of

ChemPubSoc Europe

DOI: 10.1002/chem.201600973

CHEMISTRY A European Journal Communication

Ionic Liquids

Zwitterion/Brønsted Acid Mixtures Showing Controlled Lower Critical Solution Temperature-Type Phase Changes with Water

Yuki Mieno,[a, b] Yuki Kohno,[a, b] Shohei Saita,[a, b] and Hiroyuki Ohno*[a, b]

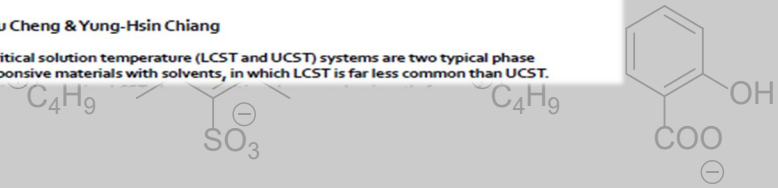
scientific reports

OPEN

Combinatorial discovery of small-molecule 1,2,3-triazolium ionic liquids exhibiting lower critical solution temperature phase transition

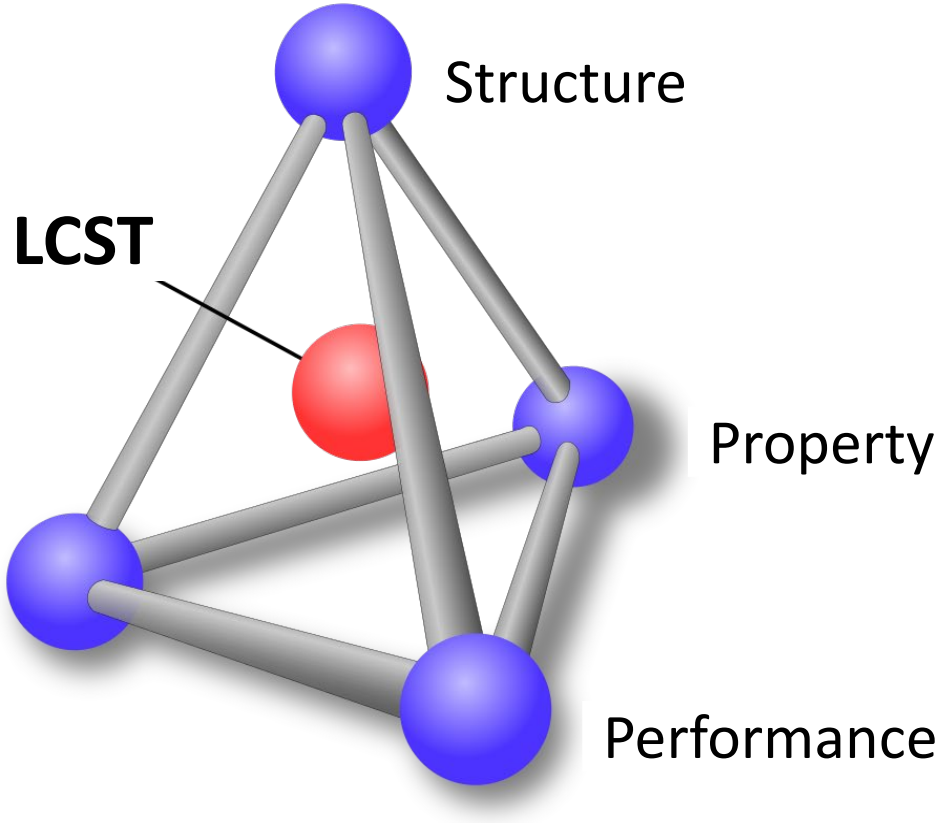
Yen-Ho Chu✉, Mou-Fu Cheng & Yung-Hsin Chiang

Both lower and upper critical solution temperature (LCST and UCST) systems are two typical phase behaviors of thermoresponsive materials with solvents, in which LCST is far less common than UCST.



Heskins et. al., *J. Macromol. Sci.*, **1968**; Ohno et. al., *Phys. Chem. Chem. Phys.*, **2012**, **14**, 5063–5070; Ohno et. al., *Chem.Eur.J.* **2016**,22,12262–12265

Lower Critical Solubility Temperature (LCST)



Ohno et. al., Phys. Chem. Chem. Phys., **2012**, 14, 5063–5070

Lower Critical Solubility Temperature (LCST)

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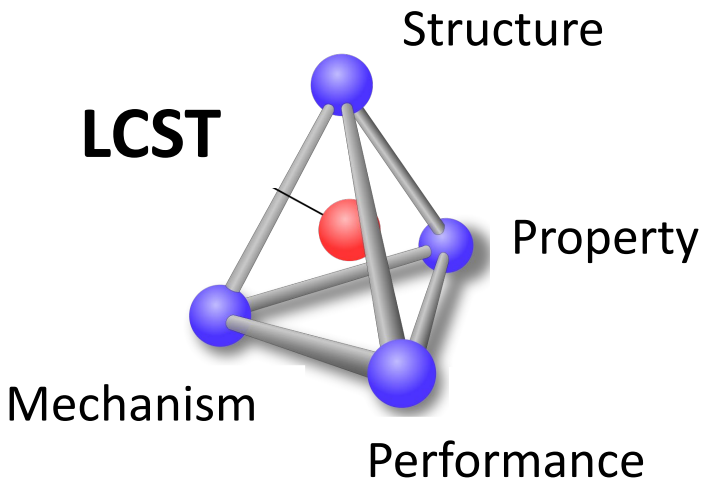
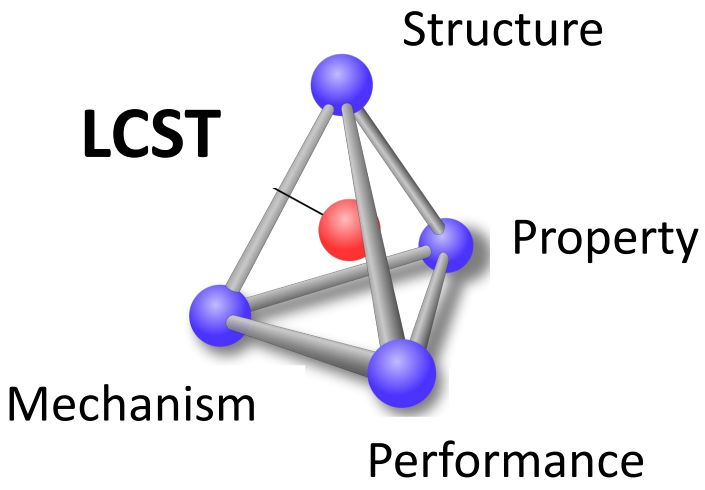


	$[P_{5555}]^+$	$[P_{4444}]^+$	$[N_{4444}]^+$
$[Tf_2N]^-$	×	×	×
BF_4^-	×	×	×
$CF_3SO_3^-$	×	×	×
$[TMBS]^-$	×	LCST	LCST
CF_3COO^-	×	LCST	○
$[DMBS]^-$	×	LCST	○
$[TsO]^-$	×	LCST	○
$[BzSO_3]^-$	×	○	○
NO_3^-	×	○	○
Br^-	×	○	○
Cl^-	×	○	○
$CH_3SO_3^-$	○	○	○

○: hydrophilic IL, ×: hydrophobic IL.

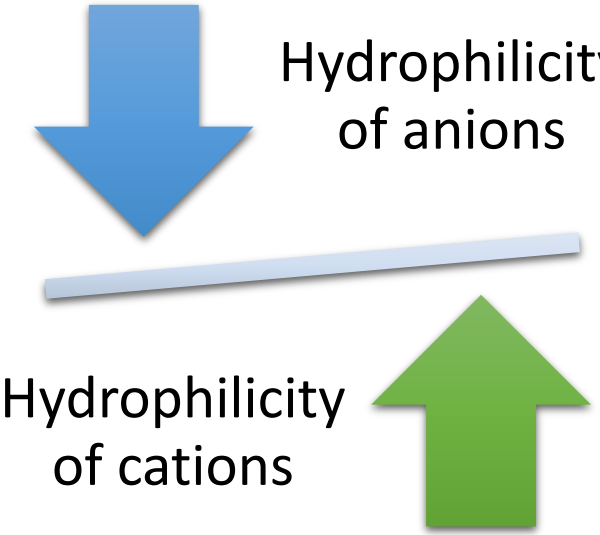
Ohno et. al., Phys. Chem. Chem. Phys., **2012**, 14, 5063–5070

Lower Critical Solubility Temperature (LCST)



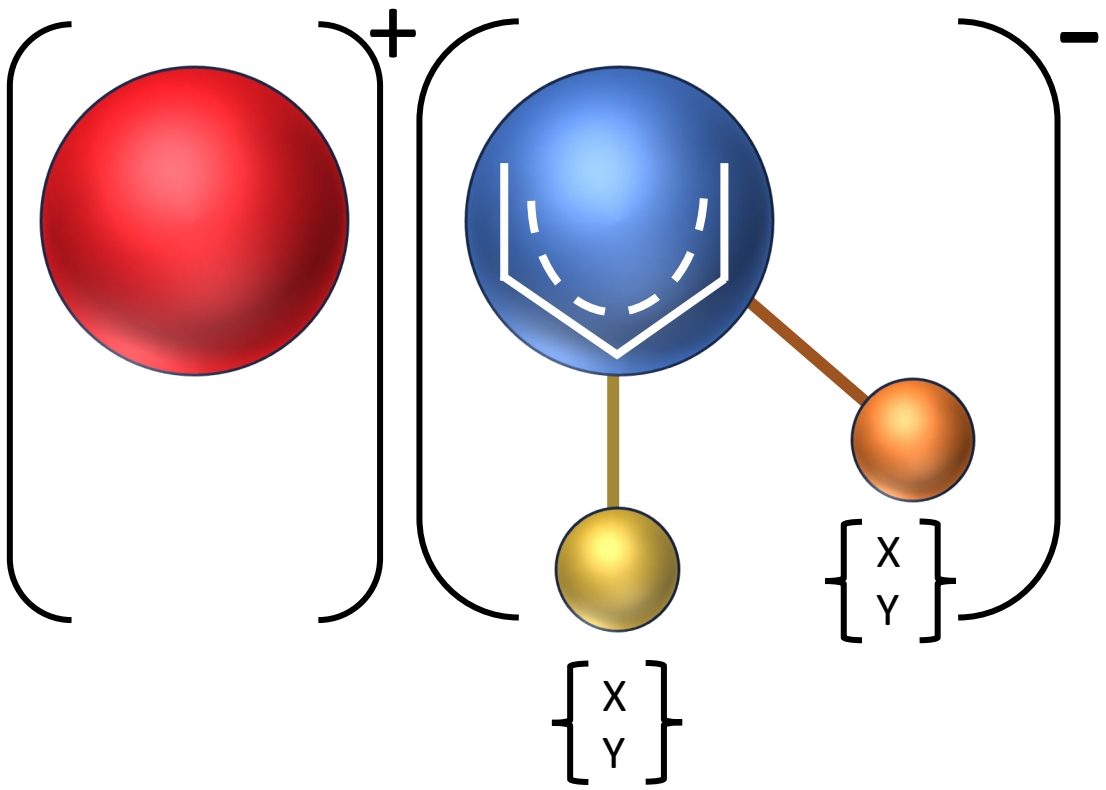
	$[P_{5555}]^+$	$[P_{4444}]^+$	$[N_{4444}]^+$
$[Tf_2N]^-$	×	×	×
BF_4^-	×	×	×
$CF_3SO_3^-$	×	×	×
$[TMBS]^-$	×	LCST	LCST
CF_3COO^-	×	LCST	○
$[DMBS]^-$	×	LCST	○
$[TsO]^-$	×	LCST	○
$[BzSO_3]^-$	×	○	○
NO_3^-	×	○	○
Br^-	×	○	○
Cl^-	×	○	○
$CH_3SO_3^-$	○	○	○

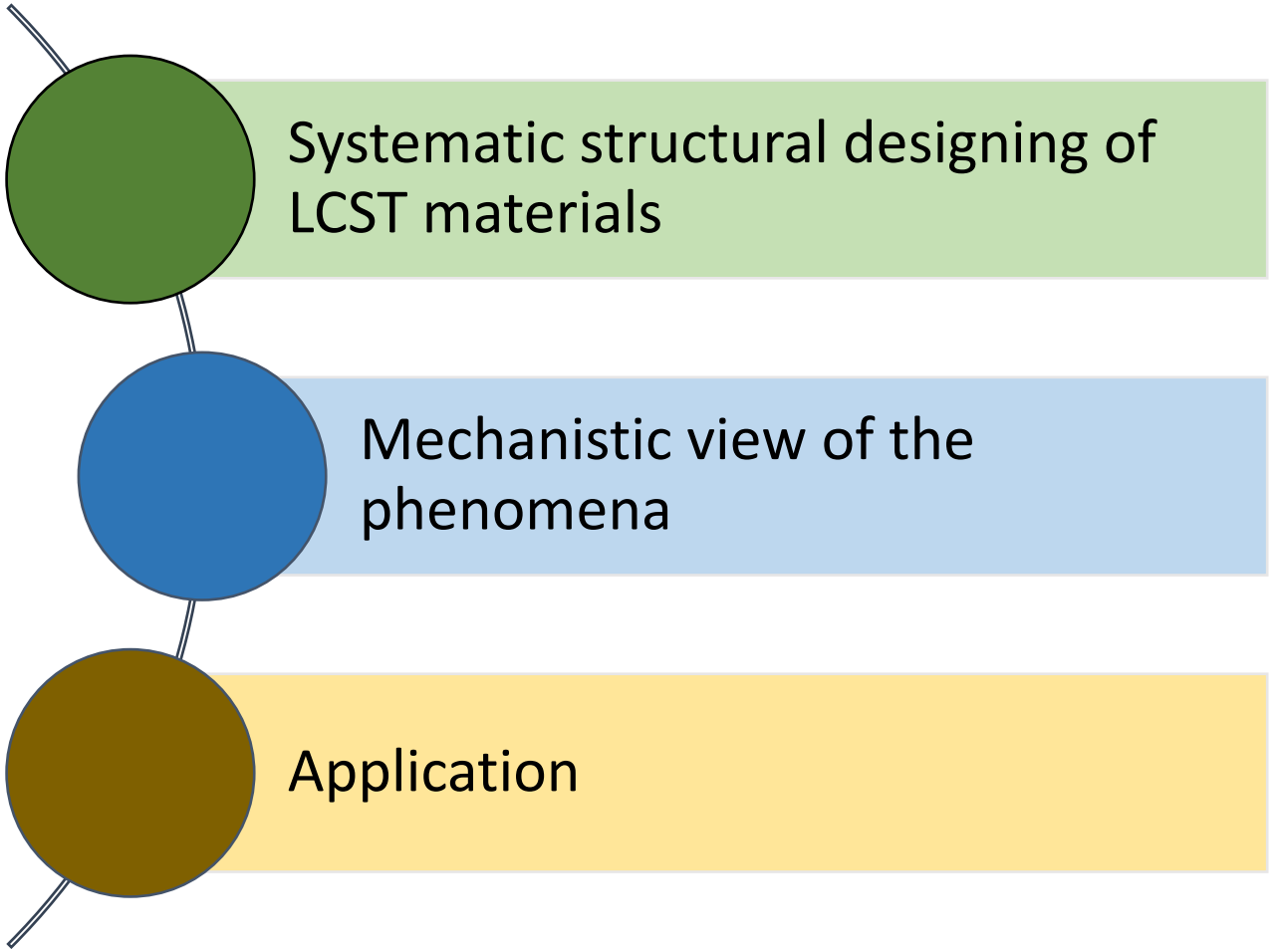
○: hydrophilic IL, ×: hydrophobic IL.



Ohno et. al., Phys. Chem. Chem. Phys., **2012**, 14, 5063–5070

Objectives





Ionic Liquids from the same family :

A result of structural modification

Synthesis of ionic liquids

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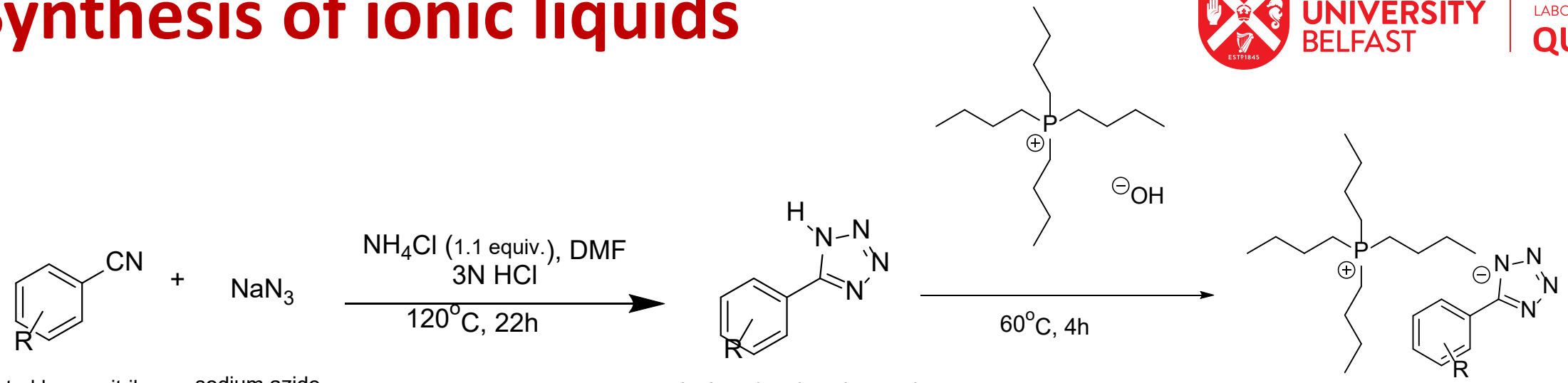


substituted benzonitrile
1 equiv.

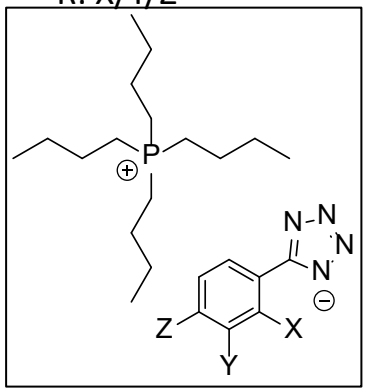
sodium azide
1.1 equiv.

substituted 5-phenyltetrazole
R= functional groups

tetrabutylphosphonium substituted 5-phenyltetrazolate

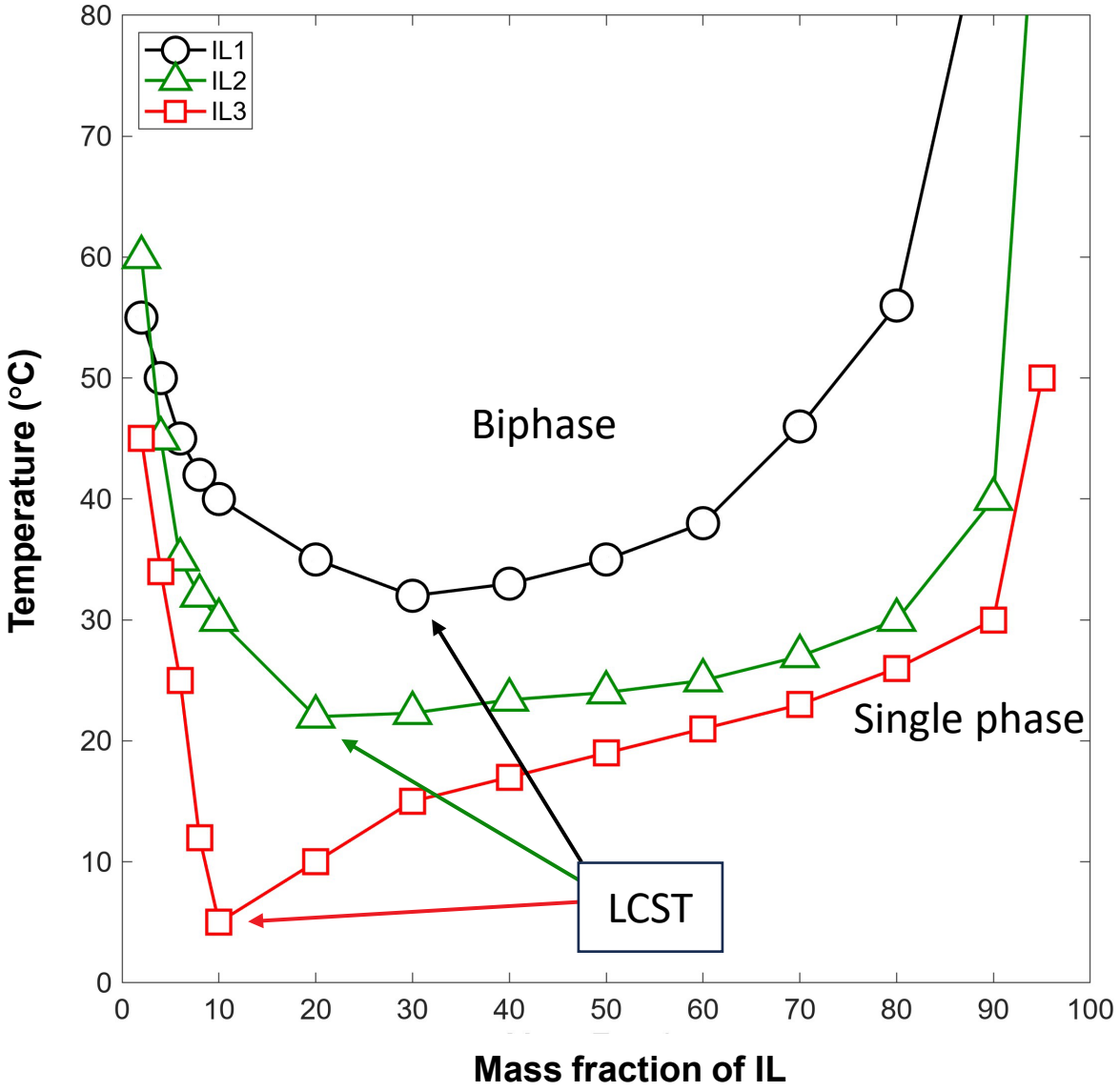
Anion modification

$[P_{4444}][R\text{-PhTet}]$
R: X/Y/Z



X	H	H	H	H	H	**CH_3**	H	**Br**	H	H	**Cl**	H	**NH_2**	H	H	**OH**	H
Y	H	H	**OCH_3**	H	**CH_3**	H	H	H	H	H	H	H	H	H	H	H	H
Z	H	**OCH_3**	H	**CH_3**	H	H	**C_2H_5**	H	**Br**	**Cl**	H	**CF_3**	H	**NH_2**	**OH**	H	**NO_2**

What do we expect?



More partial hydrophobicity

= Lower LCST (IL-3 > IL-2 > IL-1)

= Stronger ion-pair interactions

= Weaker H-bonding w/water

IL: Ionic Liquid

Non-LCST behaviour

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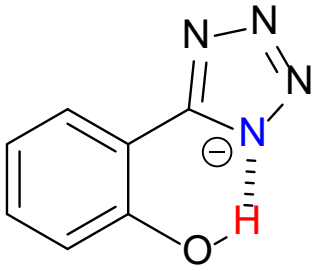
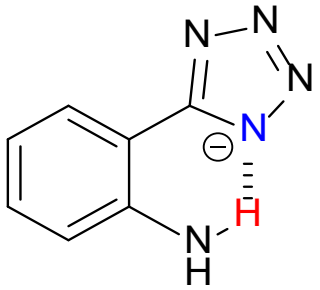
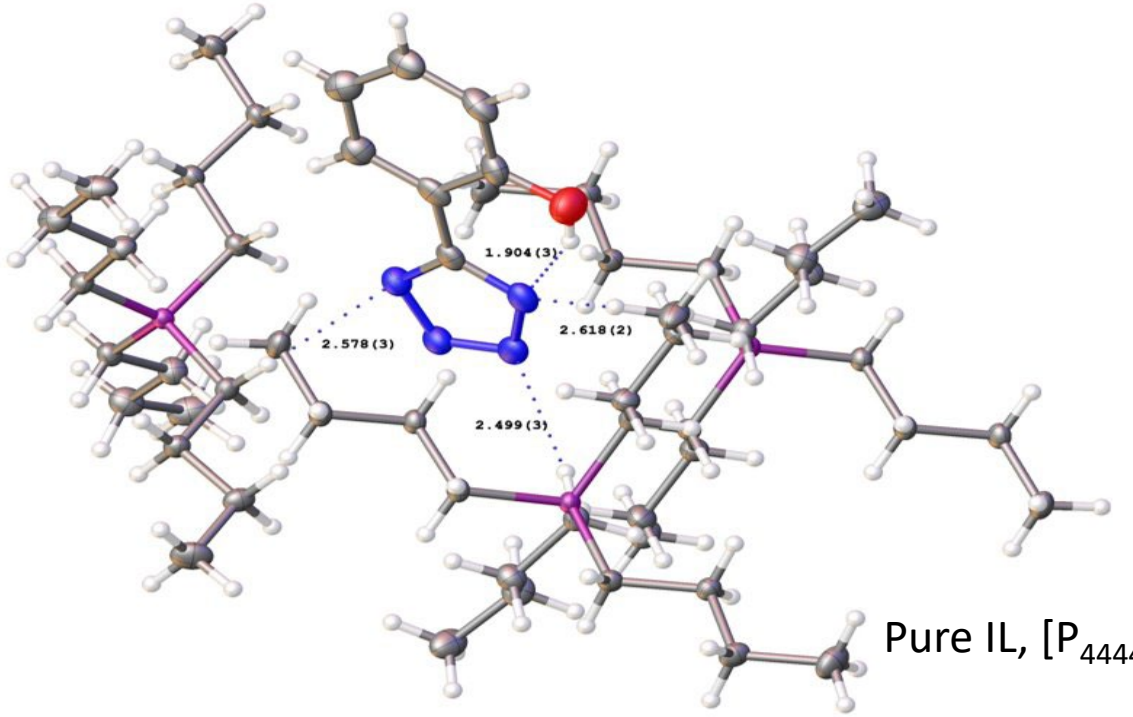


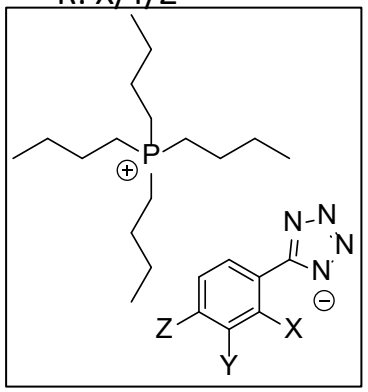


Intramolecular H-bond



Pure IL, $[P_{4444}][2\text{-OH-PhTet}]$

$[P_{4444}][R\text{-PhTet}]$
R: X/Y/Z



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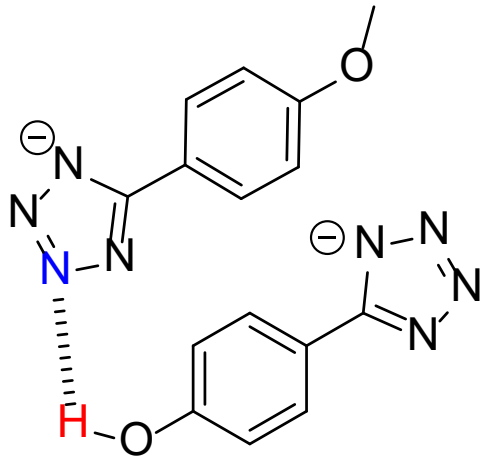
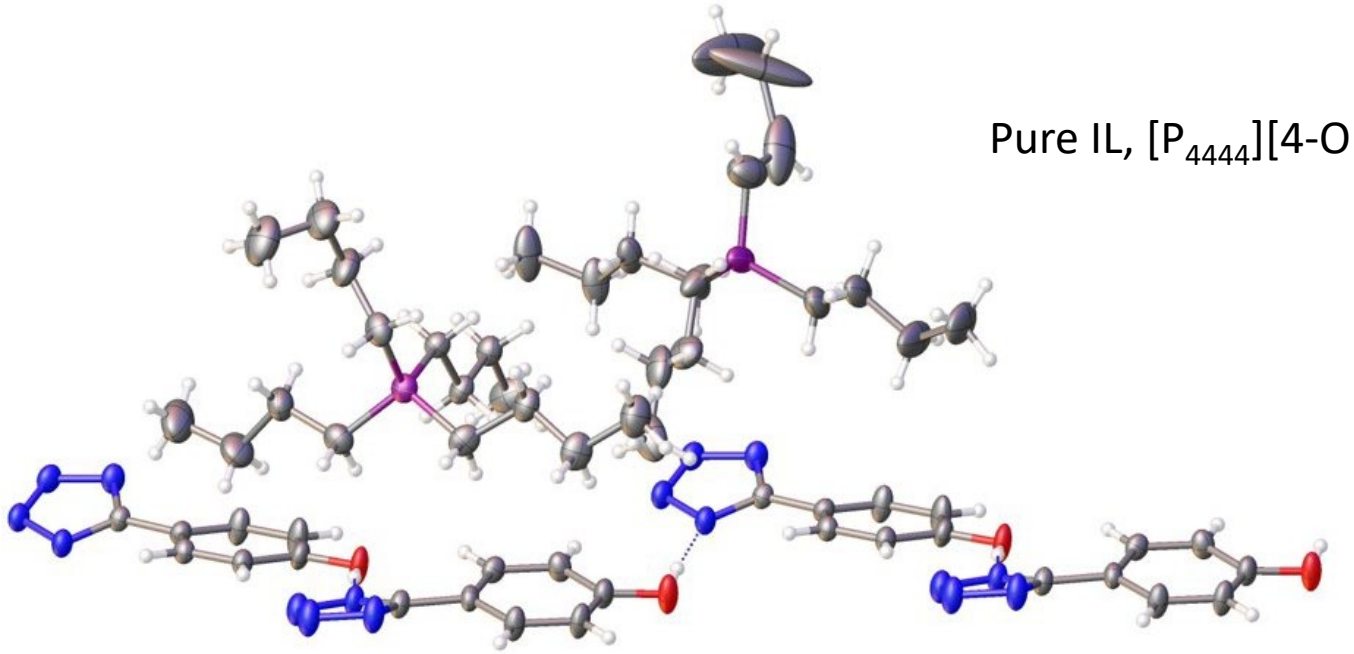
Z	H	**OCH_3**	H	**CH_3**	H	H	**C_2H_5**	H	**Br**	**Cl**	H	**CF_3**	H	**OH**	H	**NO_2**

Non-LCST behaviour

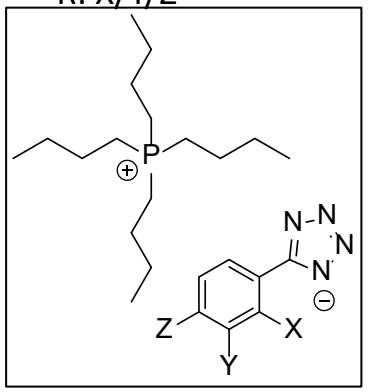


Strong anion network



Pure IL, $[P_{4444}][4\text{-OH-PhTet}]$

$[P_{4444}][R\text{-PhTet}]$
R: X/Y/Z



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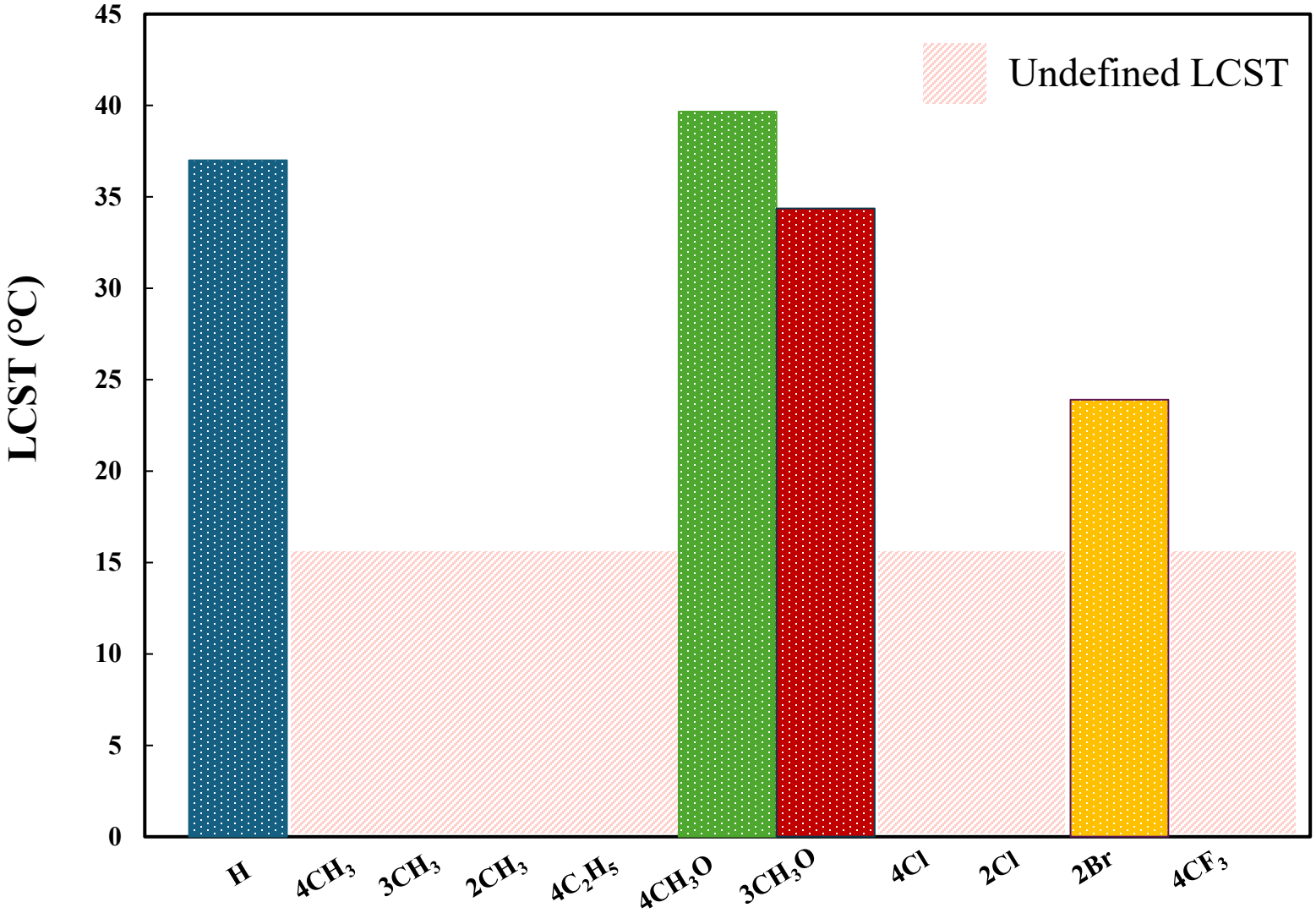
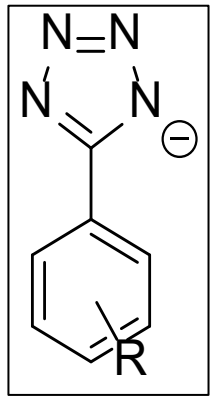
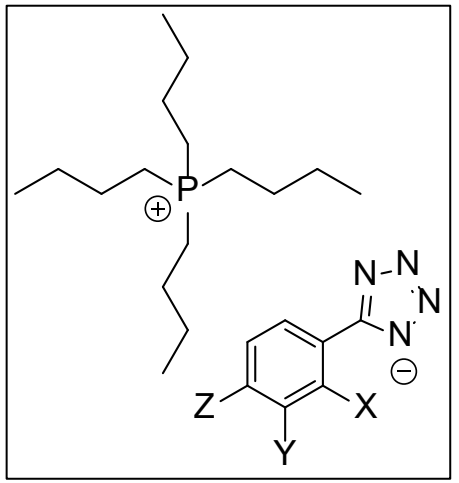
Y	H	H	**OCH_3**	H	**CH_3**	H	H	H	H	H	H	H	H	H	H	H
Z	H	**OCH_3**	H	**CH_3**	H	H	**C_2H_5**	H	**Br**	**Cl**	H	**CF_3**	H	**OH**	H	**NO_2**

Anion modification & LCST

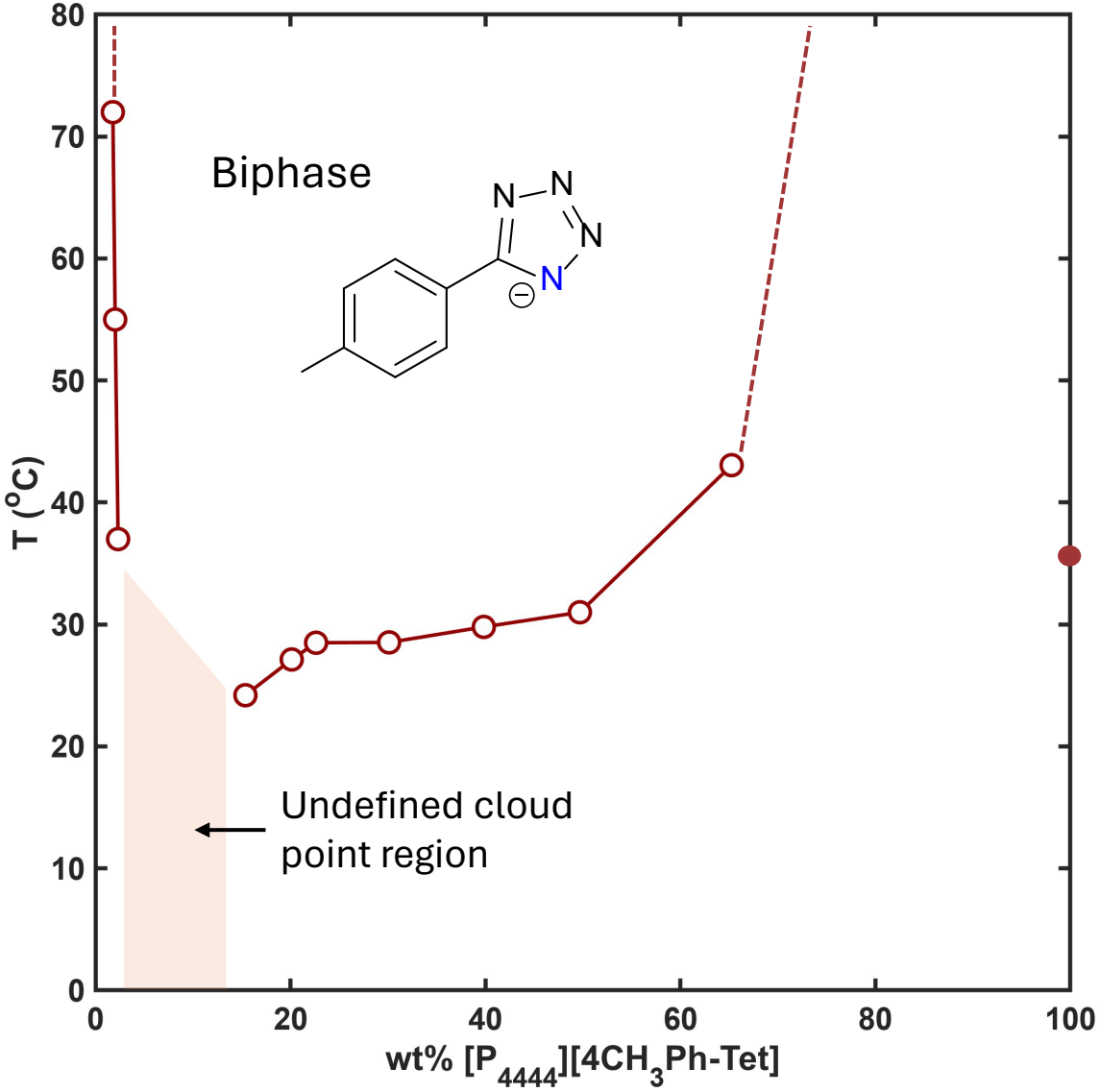


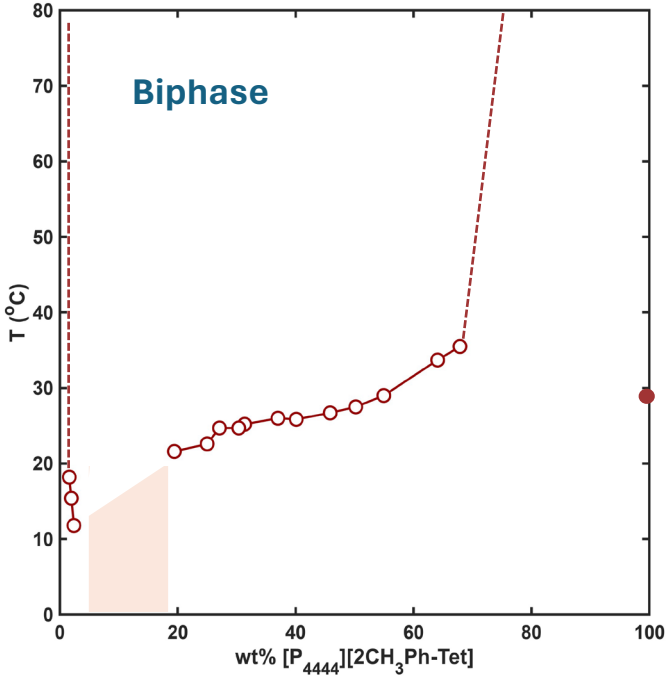


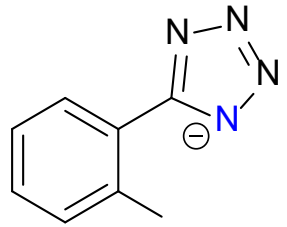


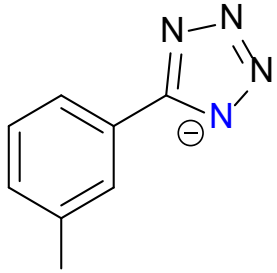
[P_{4444}][RPh-Tet]
R: X/Y/Z

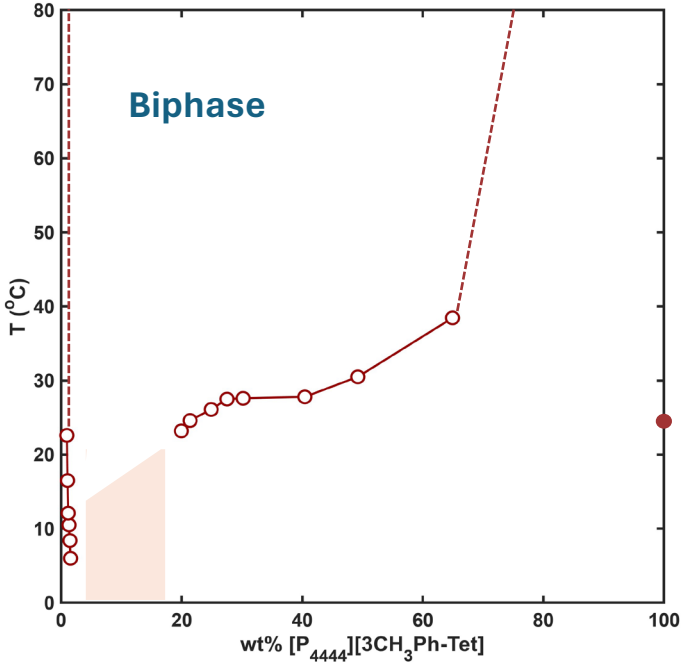
Temperature-composition phase diagram for solutions of $[P_{4444}][CH_3PhTet]$ + H_2O as a function of the weight percentage of IL





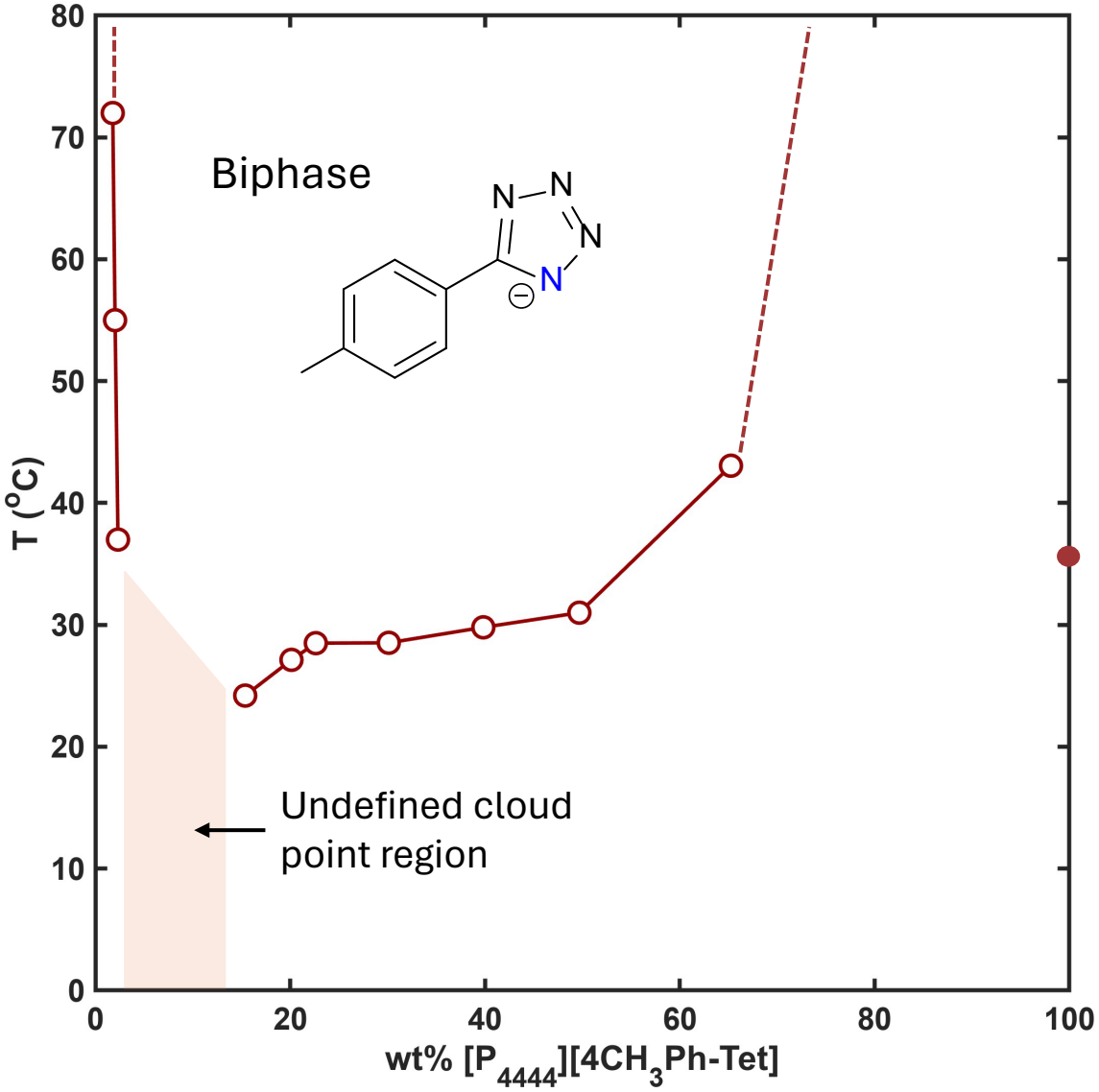


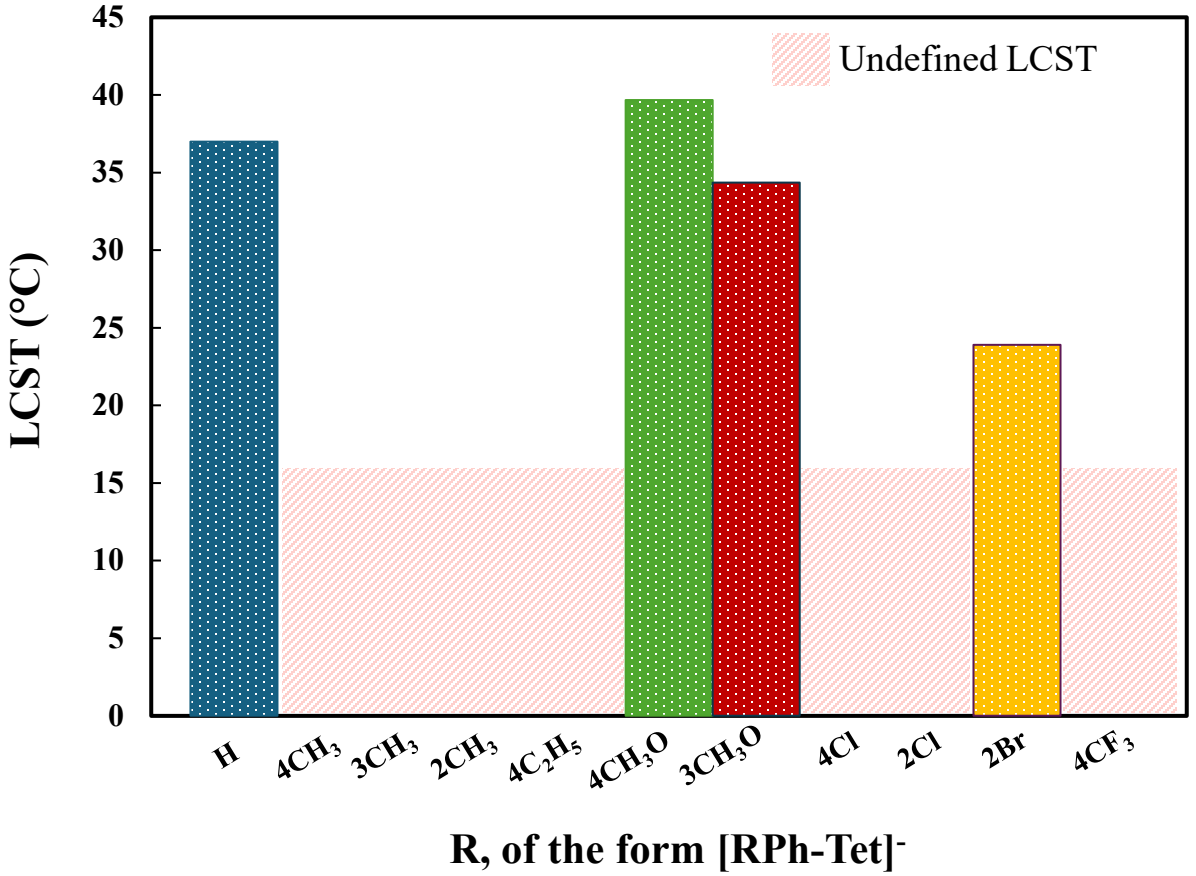




Dotted lines indicate that samples were measured until 80°C, but no distinct phase separation (cloudiness) was observed

Temperature-composition phase diagram for solutions of $[P_{4444}][CH_3PhTet] + H_2O$ as a function of the weight percentage of IL





Dotted lines indicate that samples were measured until 80°C, but no distinct phase separation (cloudiness) was observed

LCST- unstable or metastable?

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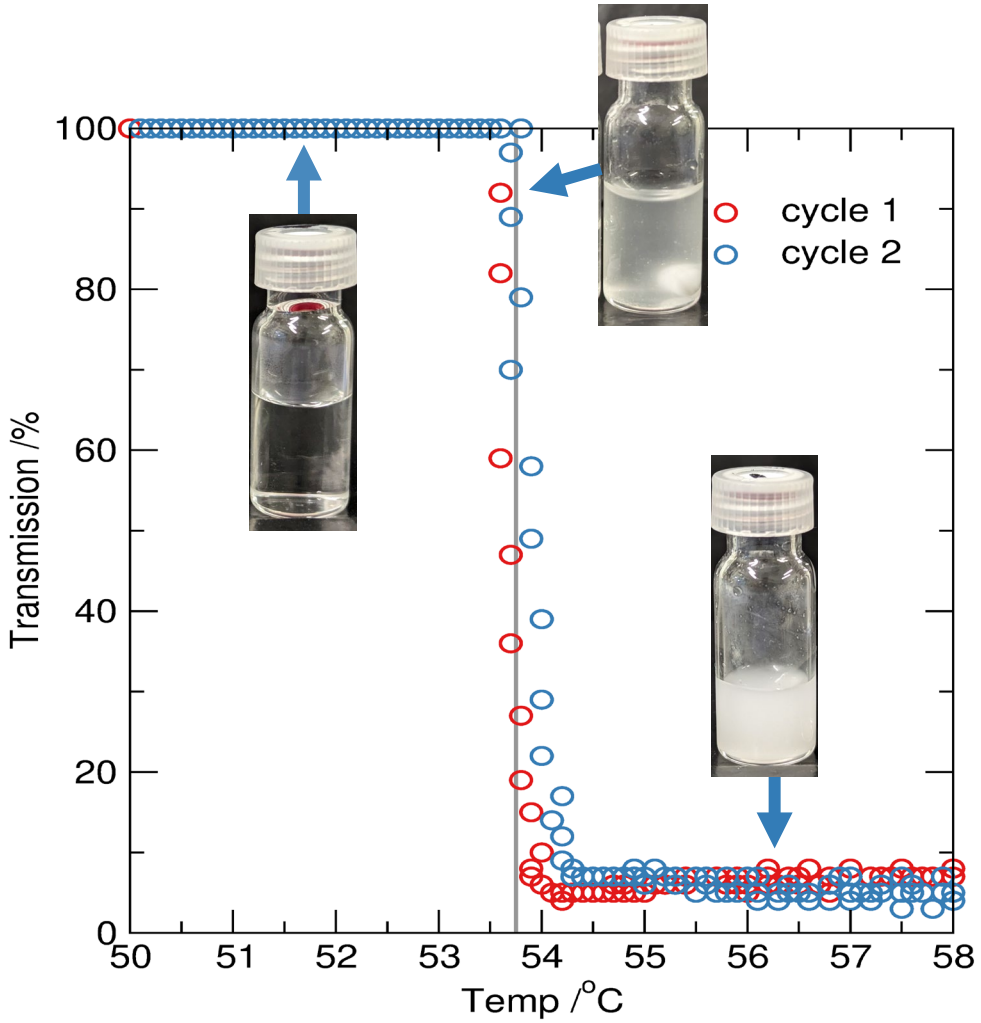

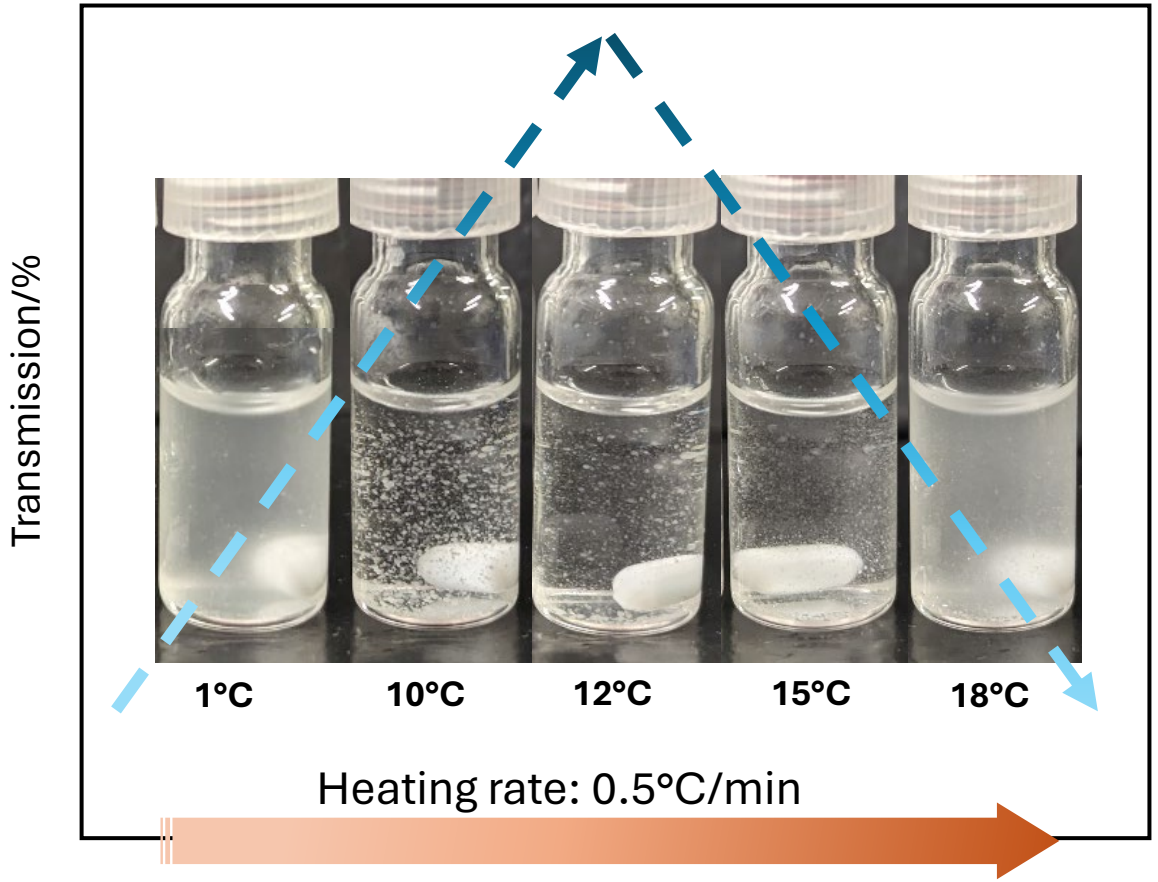

Stable LCST transition in IL/H_2O mixtures

LCST- unstable or metastable?

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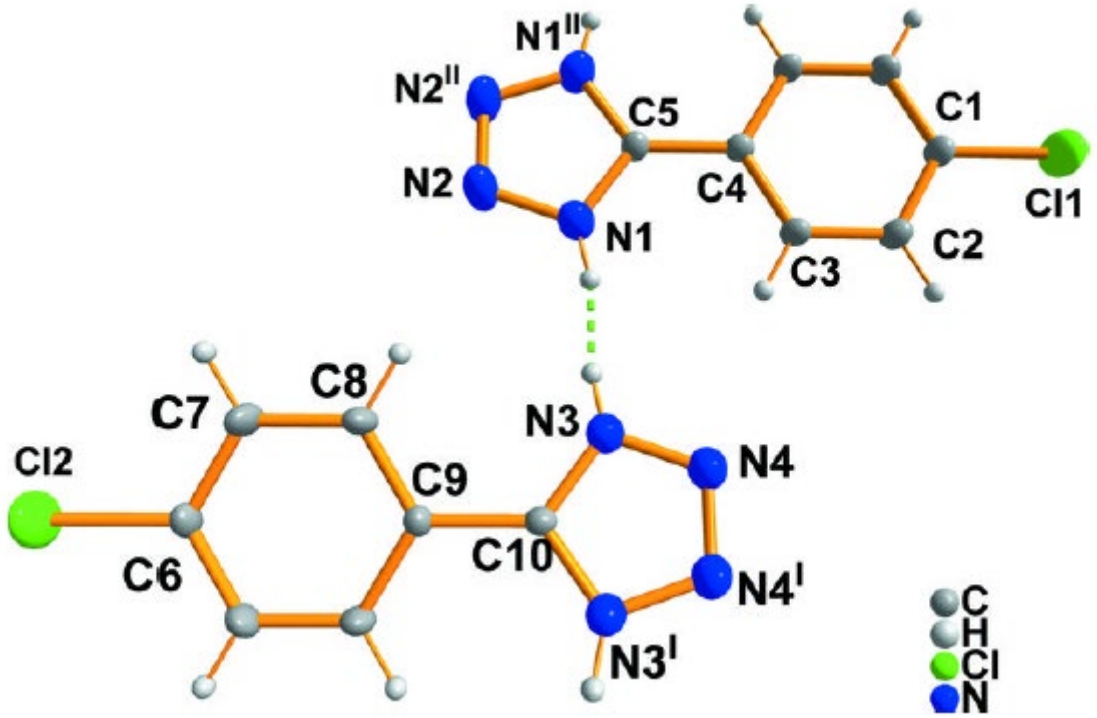

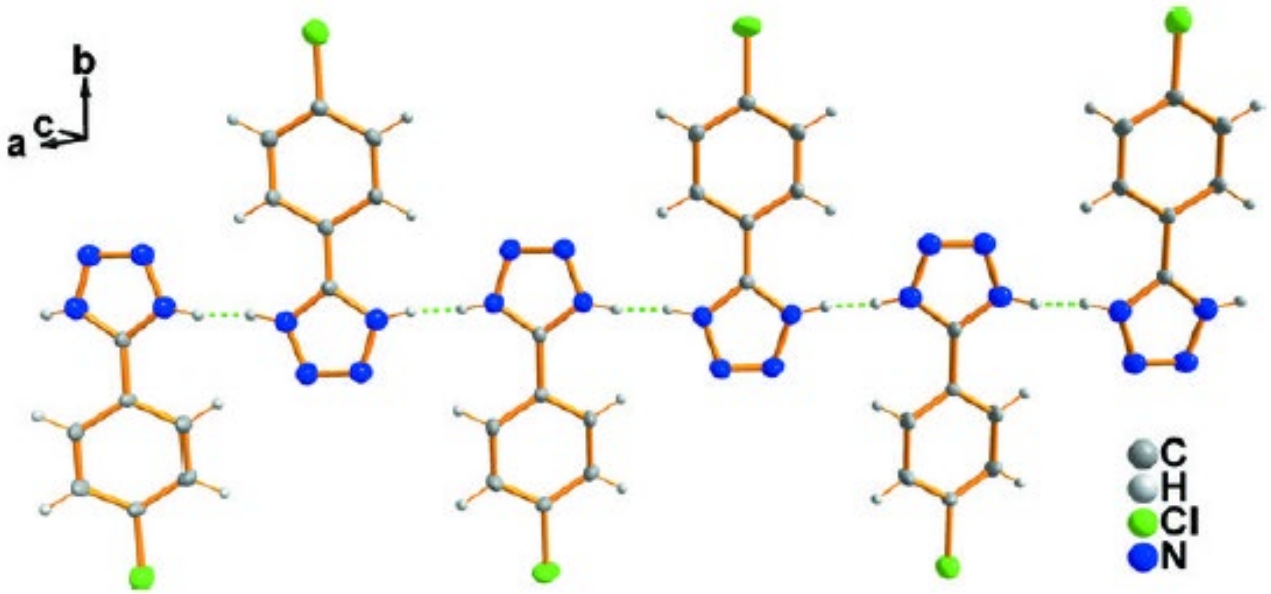

The molecular structure of 5(4-chlorophenyl-*1H*-tetrazole), showing displacement ellipsoids at the 50% probability level for non-H atoms. *Dashed lines indicate the hydrogen bonds*.

A partial packing view, showing one-dimensional chain structure. *Dashed lines indicate the hydrogen bonds*.

Acta Cryst. (**2010**). E66, o742

LCST- unstable or metastable?

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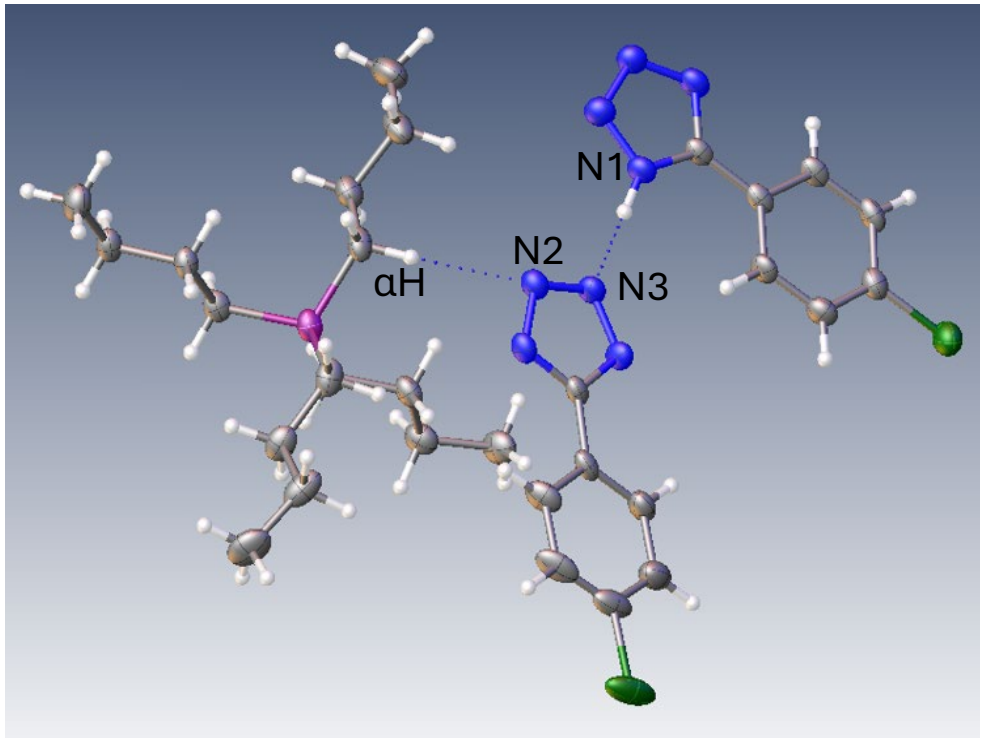
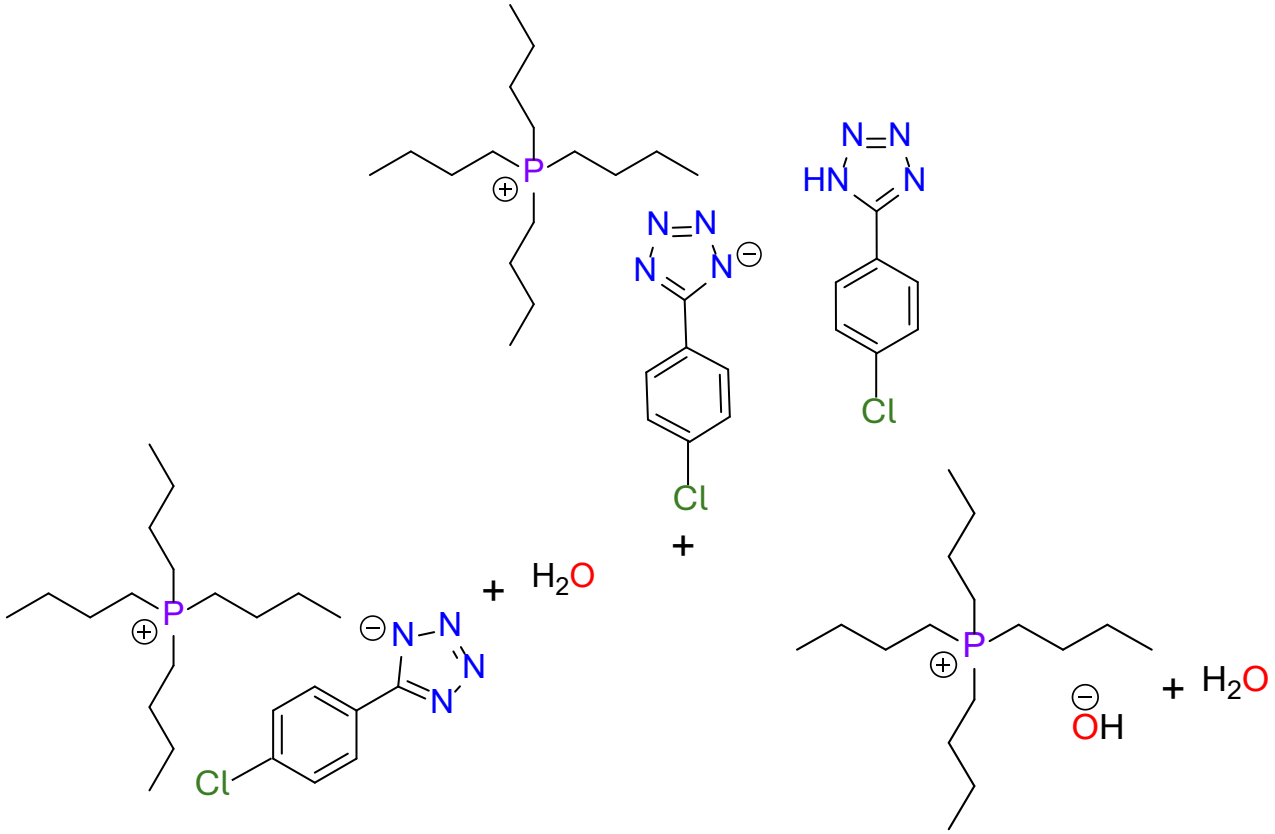
Crystal structure from 55.33wt% $[P_{4444}][4ClPhTet]/H_2O$





- 1 Cation-anion pair : H-bond between αH-N2
- 1 protonated 5-phenyltetrazole : H-bond between NH of the tetrazole and N3 of the tetrazolate anion

LCST- unstable or metastable?

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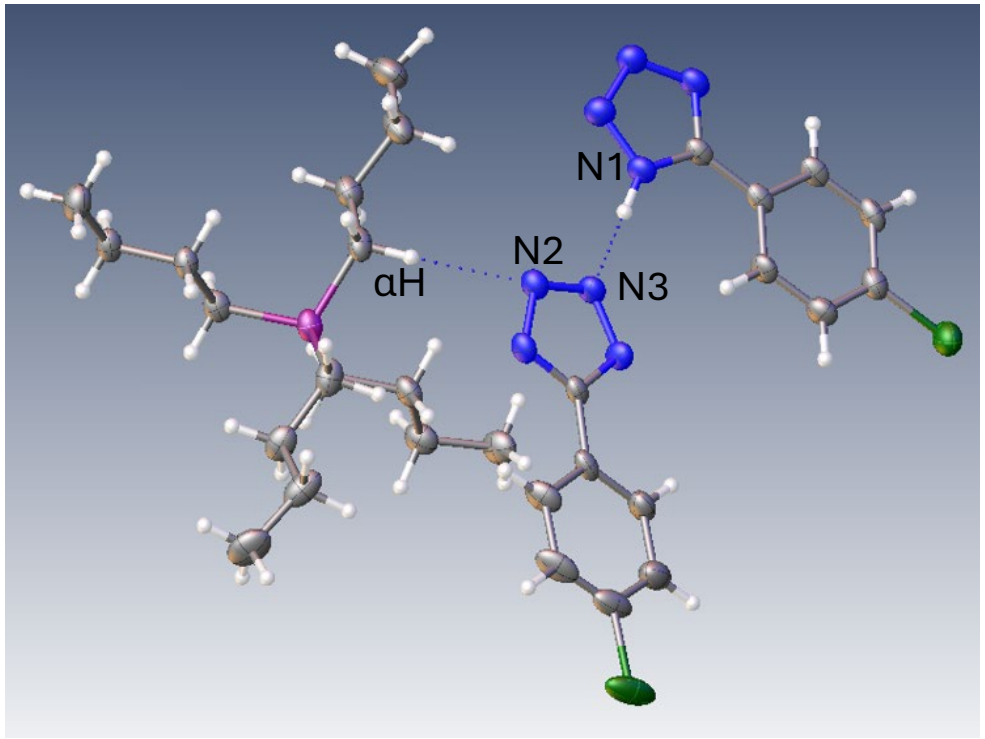

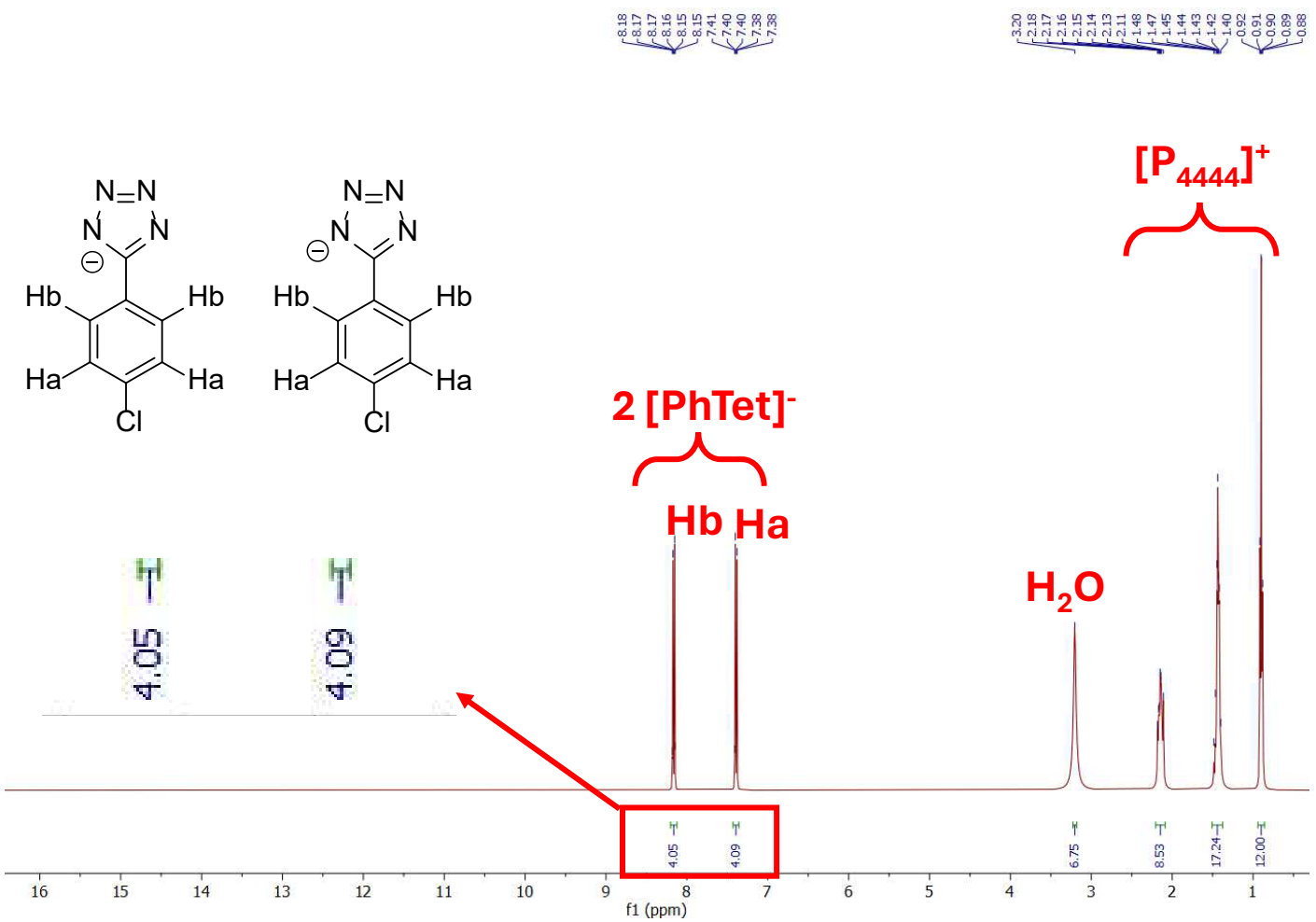

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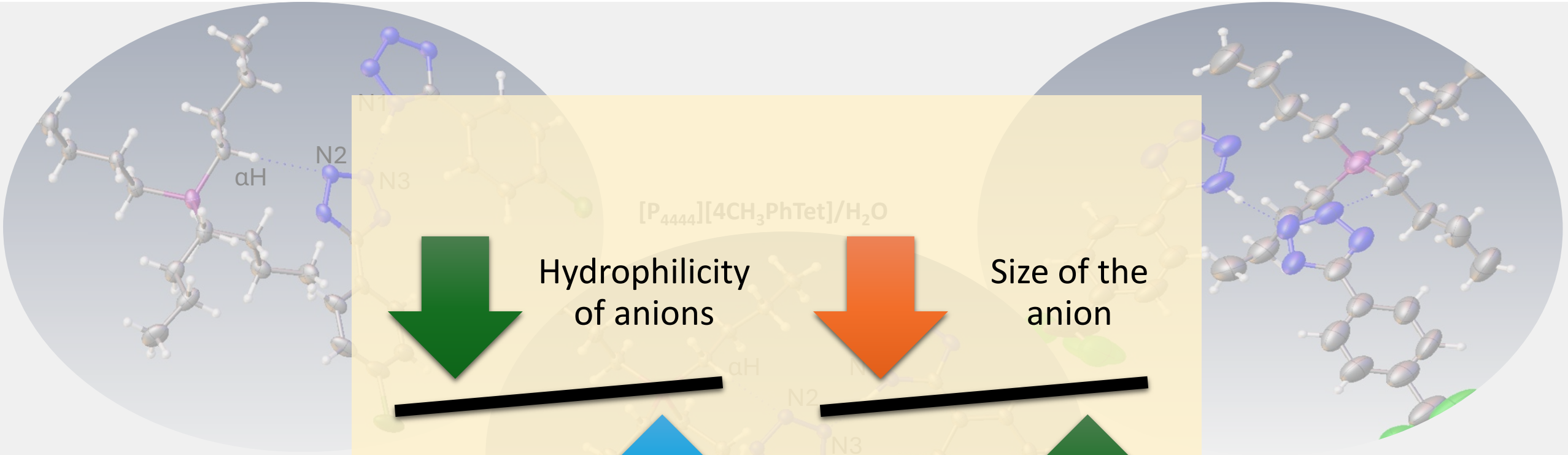

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Fine tuning LCST

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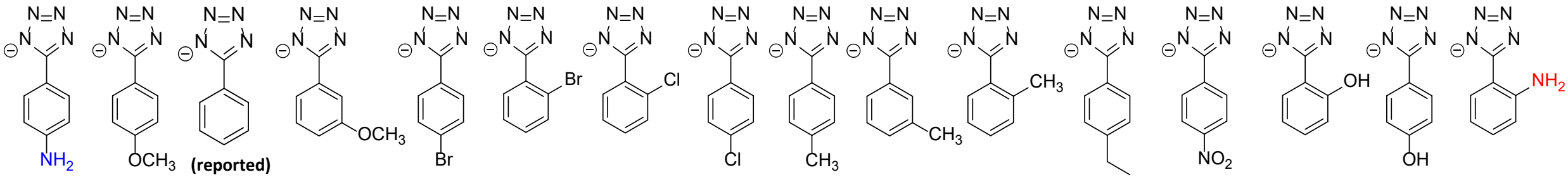
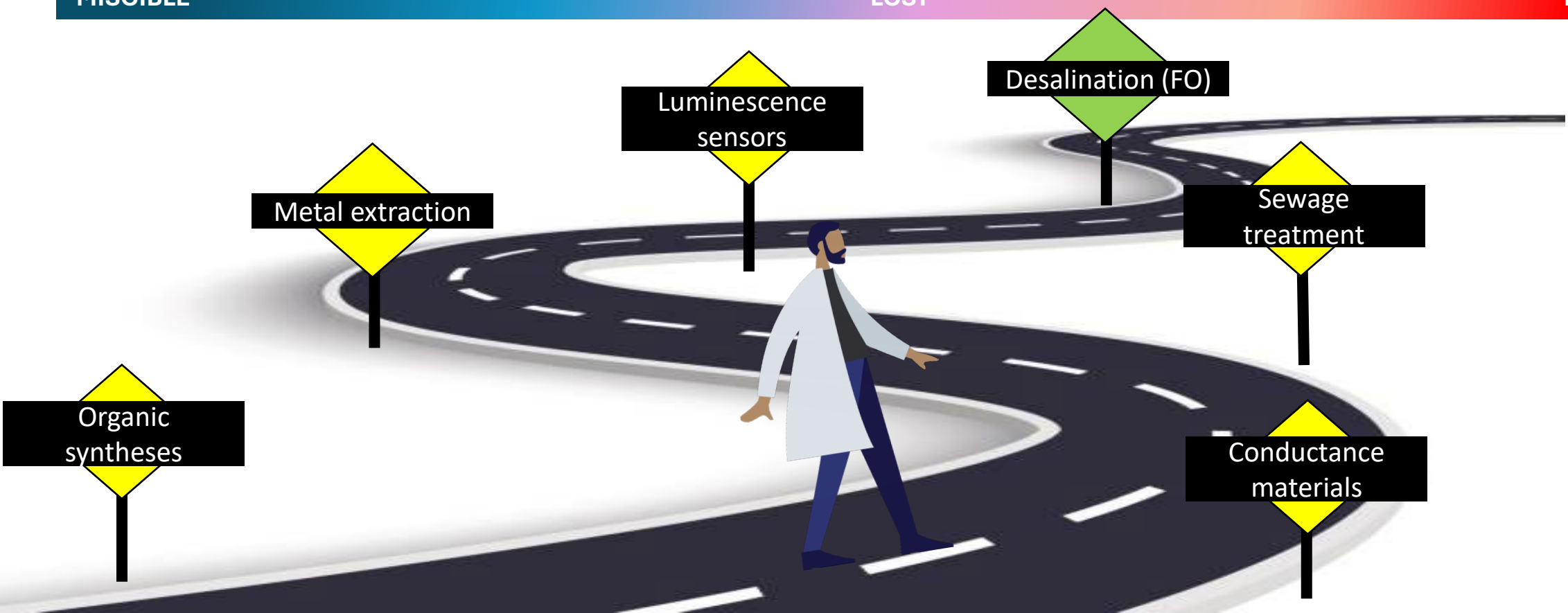


MISCIBLE — LCST — IMMISCIBLE



Conclusion & future works

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1. Methodical synthesis approach has been employed, generating ILs to understand their structure-property relationship to the LCST behaviour.

2. Tunability of LCST behaviour through structural modification and its enormous potential in industrial applications.

3. Comparative study on Dicationic Ionic liquids,

4. Calculate Hydrogen-bond basicity/pKa/ß-values for the anions,

5. Thermo-responsive hydrogels and their prospectives in FO processes.

Acknowledgements

- Professor John Holbrey
- Dr. Leila Moura
- Professor Peter Nockemann
- Everybody else in the QUILL lab, QUB