Organic Salt Hydrates as Phase Change Materials

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Overview

The effective utilisation of solar thermal energy in commercial and residential settings is an important step in the decarbonization of energy supply chains[1].

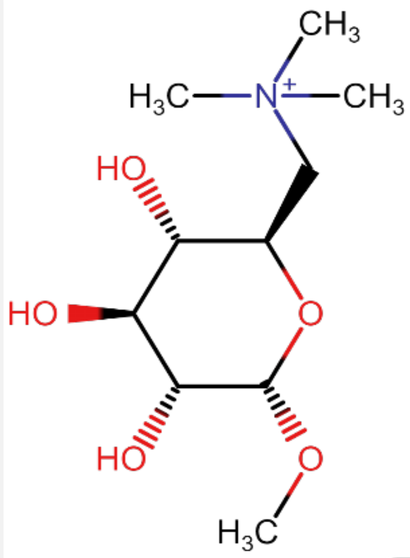
Phase change materials (PCMs) are substances capable of absorbing and storing thermal energy upon melting, and releasing said energy when allowed to re-solidify[2]. The energy a PCM is capable of storing and releasing is expressed by its **enthalpies of fusion, ΔH_f.**

Many substances with high ΔH_f, such as certain common sugar alcohols are prohibited from a more widespread use due to their high degree of **supercooling**[3], that is, the tendency to crystallize at temperatures **(T_c)** far below their melting points (T_m)[4].

The study of salts of the **N(-6-deoxy-1-O-methoxy-α-D-glucopyranosido) N,N,N-trimethylammonium ([MGPTMA]$^+$)** cation, and other **ionic monosaccharide derivatives** as potential PCMs arose from the desire to seek materials with the deemed likely to possess the **high ΔH_f** s as the similarly hydroxyl-rich sugar alcohols, yet the **minimal supercooling** that is characteristic many ionic compounds.

Project Aims:

- To study the thermal properties (**melting point**, T_m, and **enthalpy of fusion, ΔH_f**) and the **degree of supercooling ($\Delta T = T_m - T_c$)** of a series of salts of the [MGPTMA] cation
- To characterise these materials' crystal structures in order to to better ascertain the relationship between their thermal properties and the quantitative and qualitative intermolecular bonding

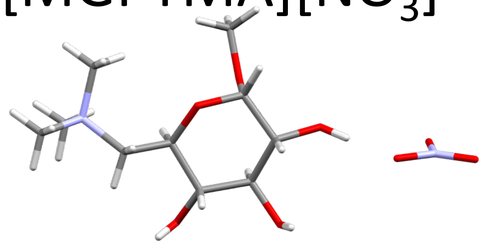


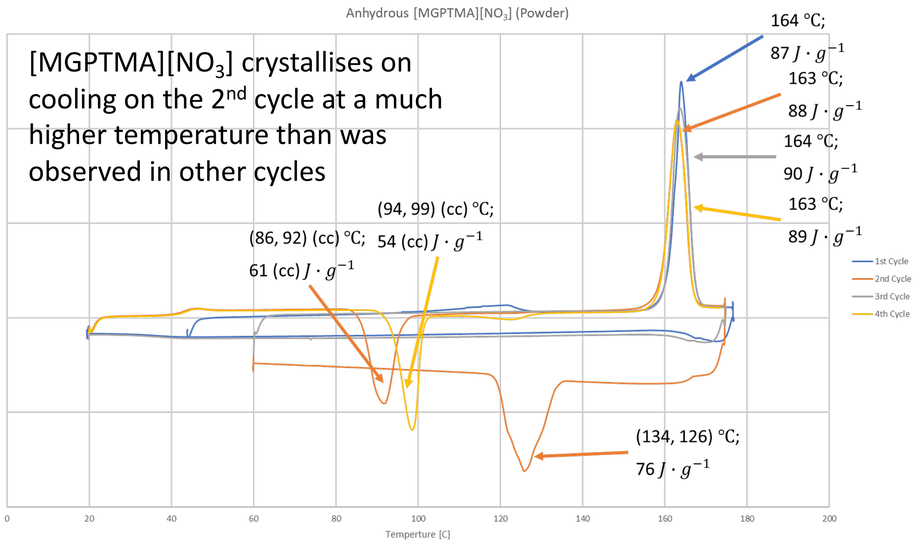
N(-6-deoxy-1-O-methoxy-α-D-glucopyranosido) N,N,N-trimethylammonium ([MGPTMA]$^+$) ion

Thermophysical properties of [MGPTMA] salts

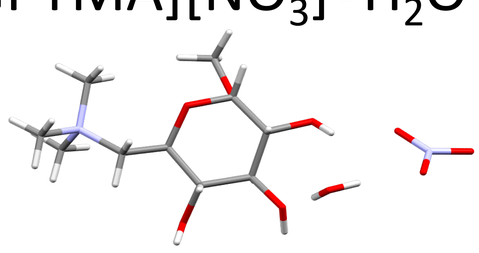
Anion	T_m, °C ± 2 °C	ΔH_f, J/g ± 5%	Degree of Supercooling, °C ± 2 °C
$[NO_3]^-$	136	88	32
$[NO_3]^- \bullet H_2O$	163	107	29
$[CH_3SO_3]^-$	199	38	
$[BF_4]^-$	99	44	
Br^-	233	109	N/A
$Br^- \bullet H_2O$			

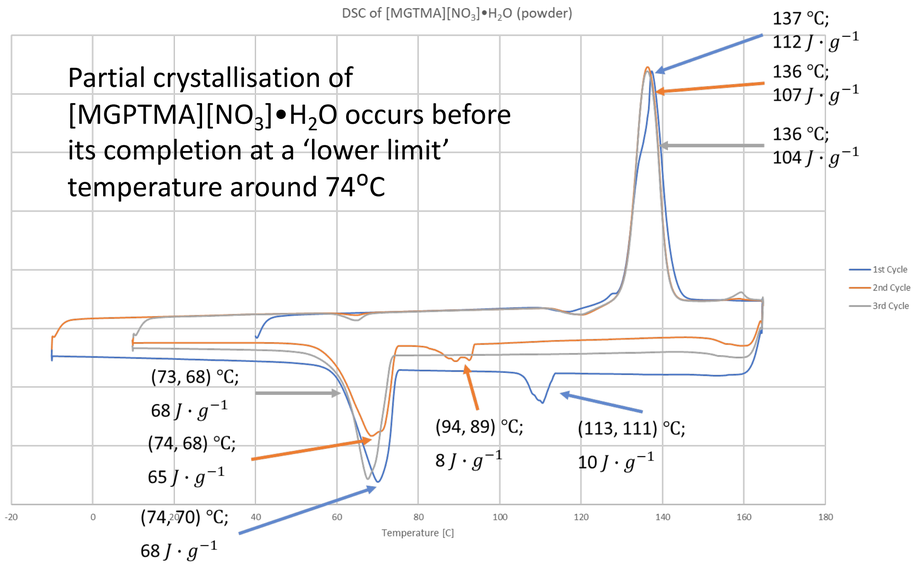
[MGPTMA][NO_3]



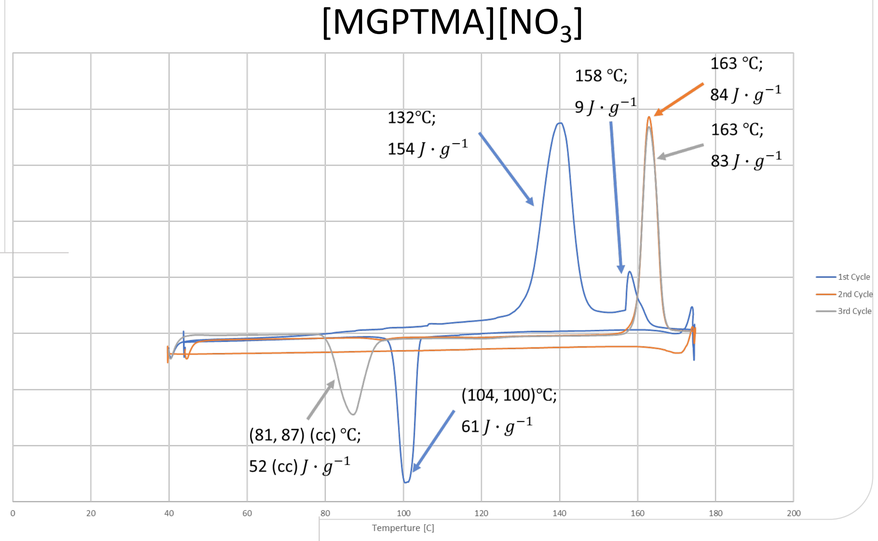


[MGPTMA][NO_3]•H_2O



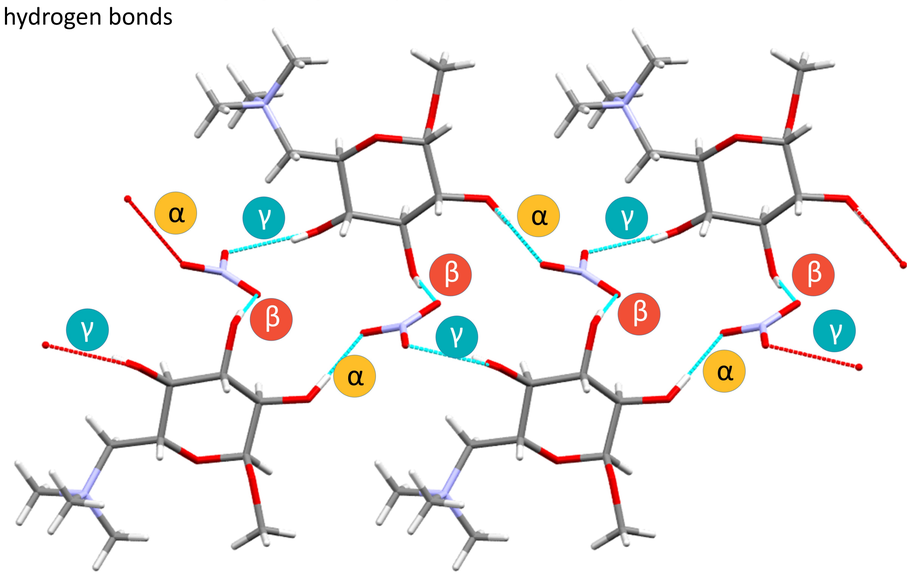


Conversion of [MGPTMA][NO_3]•H_2O to [MGPTMA][NO_3]



Crystallographic analysis

Section of a single linear 'chain' that comprises the crystalline solid state of **[MGPTMA][NO3]**, highlighting the **topological connectivity** of its intermolecular hydrogen bonds

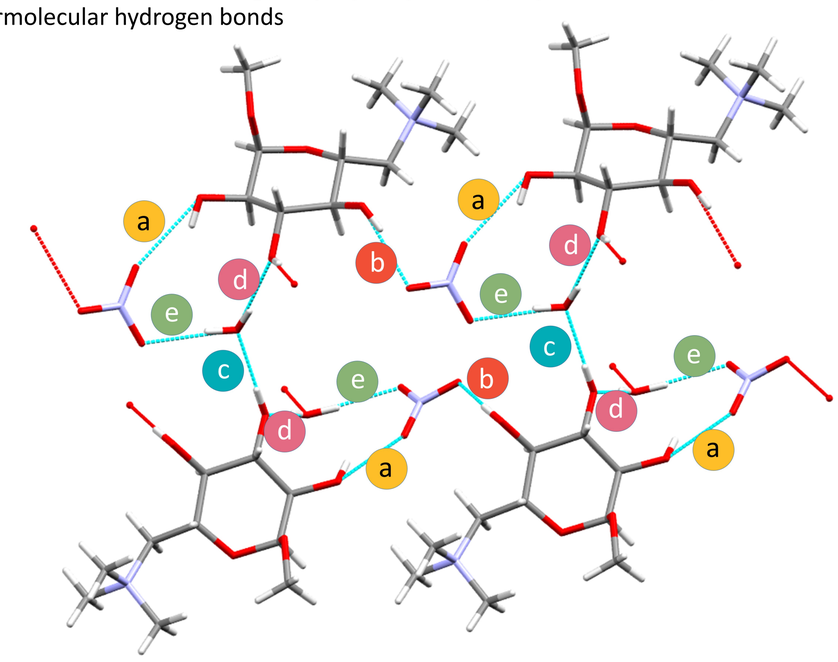


Unique Bond	O···O Bond Length (Å)	O···O Bond Length (Å)	∠OOH Bond Angle (°)
α C(2)OH···ON	2.840	1.973	7.59
β C(3)OH···ON	2.952	2.091	3.97
γ C(4)OH···ON	2.716	1.965	12.75

In the case of both crystal structures:

- The favourable crystallisation behaviour is suspected to arise from the **strong hydrogen bonds (of minimal bond angle)** the nitrate anions are capable of sustaining with the MGPTMA cations' 'free' hydroxyl groups
- The **relative simplicity** of the topological connectivity of the networks formed by these intermolecular hydrogen bonds may also have a relationship to **favourable crystallisation kinetics**, assisting in **minimising supercooling**

Section of the 2D network of orthogonal 'chains' that comprise the crystalline solid state of **[MGPTMA][NO3]•H_2O**, highlighting the **topological connectivity** of its intermolecular hydrogen bonds



Unique Bond	O···O Bond Length (Å)	O···O Bond Length (Å)	∠OOH Bond Angle (°)
a C(2)OH···ON	2.695	2.002	25.95
b C(4)OH···ON	2.753	1.954	12.40
c C(3)OH···O(w)H2	2.794	1.939	5.41
d O(w)H···OC(3)	2.913	2.092	5.61
e O(W)H···ON	2.794	1.935	4.75

•This same structural motif (and near exact same topological connectivity) was also observed in the monohydrate salts **[MGPTMA]Br•H_2O** and **β-[MGPTMA][BF_4]•H_2O**. This highlights the importance bond strength and angle plays in determining a material's thermophysical properties, despite comparable crystal structures and connectivity.

Conclusions:

- The best thermal properties were found in both anhydrous **[MGPTMA][NO_3]** and its monohydrate, **[MGPTMA][NO_3]•H_2O**.
- **[MGPTMA][NO_3]•H_2O** may perhaps be the first known example of an **'organic salt hydrate' PCM**. Organic salt hydrates have possible advantages over the widely-utilised Inorganic Salt Hydrates.
- **Strong intermolecular hydrogen bonds** correlate to a **high enthalpy of fusion**, but a **minimised supercooling** correlates to the **ease with which these bonds are re-formed** upon crystallisation. These should be the guiding principals for future PCM design

Literature Cited

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