Triazolium based salts as phase change materials for thermal energy storage

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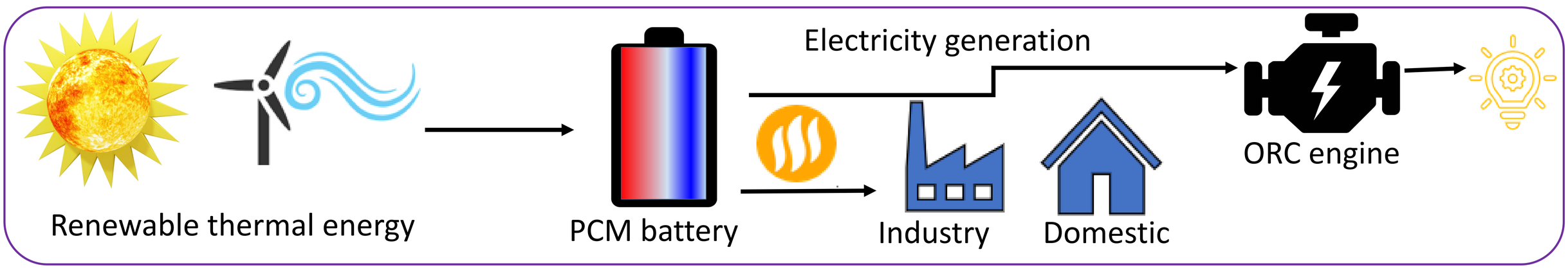
Phase change materials (PCMs) which undergo reversible phase transition at a definite temperature and have high enthalpy of fusion ($\triangle H_f$) can effectively store thermal energy for later use either directly as heat or for electricity generation in the organic Rankine cycle (ORC). Intermediate temperature PCMs (T_m =100-200 °C) are desirable as this temperature is regularly achieved in vacuum tube solar collectors. While traditional PCMs suffer from various drawbacks like thermal instability, low cyclability, low thermal conductivity, and high supercooling, there is immense scope to design better PCMs based on ionic liquids. This work aims:

1. To study a series of 1,2,4-triazolium based organic salts as potential PCMs and
2. Investigate the molecular level interactions and determine the driving forces of high heat of fusion in organic salts.

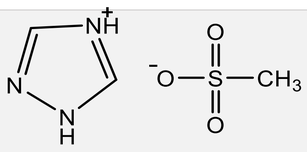


Thermal data

Table 1. Thermal data for 1,2,4-triazolium (1,2,4-TAM) salts as PCM.

Material	Melting point (T_m) °C ± 1 °C	Heat of fusion ($\triangle H_f$) J.g^{-1} ± 5%	Decomposition onset (T_d) °C ± 2 °C
[1,2,4-TAM]Cl	156^{S-S}, 173	19^{S-S}, 89	197
[1,2,4-TAM][HSO_4]	97	95	272
[1,2,4-TAM][CH_3SO_3]	137	140	286
[1,2,4-TAM][$C_2H_5SO_3$]	93	68	294
[1,2,4-TAM][CF_3SO_3]	169	126	356
[1,2,4-TAM][$C_6H_5SO_3$]	144	134	323

s-s solid-solid transitions



[1,2,4-TAM][CH_3SO_3]

Crystallographic analysis

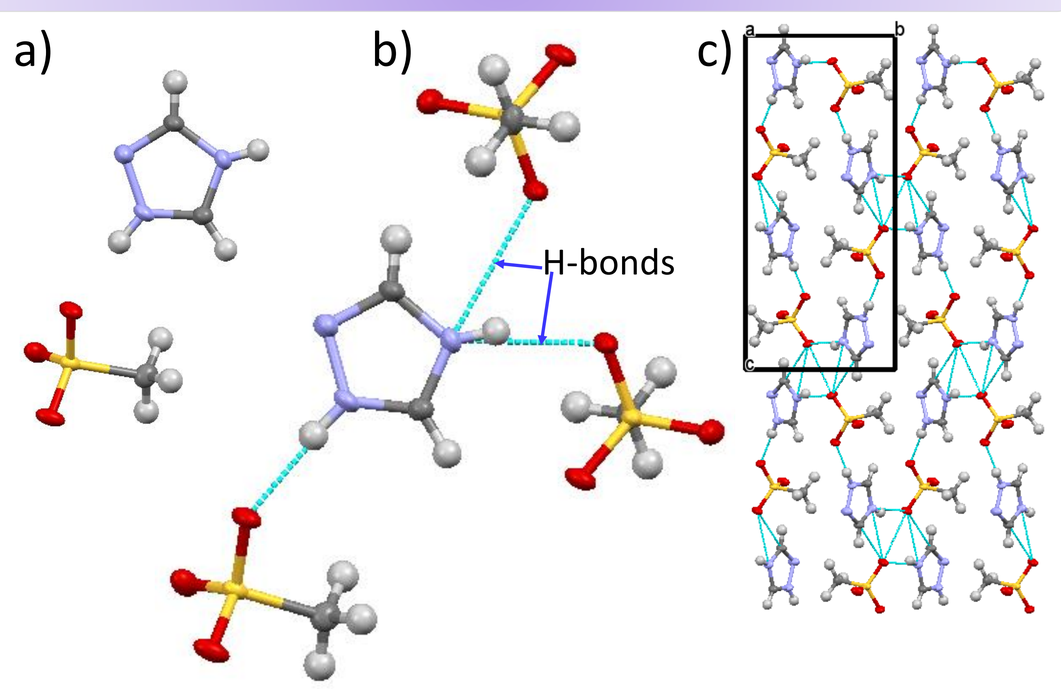


Figure 1. Crystal structure of 1,2,4-triazolium mesylate[1] a) asymmetric unit (b) H-bond among ions (c) crystal packing view along a. The presence of strong H-bonds (short and linear) make the compound absorb large amount of energy during phase transition leading to high $\triangle H_f$.

Hirshfeld analysis

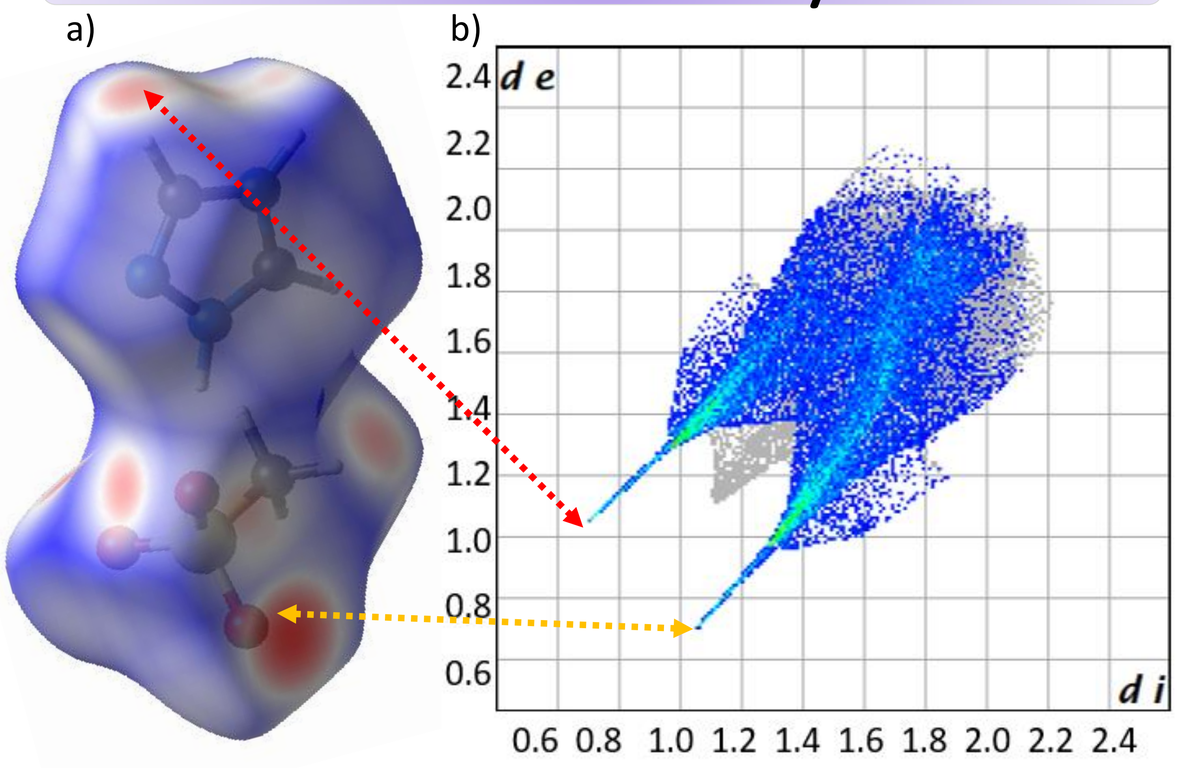


Figure 2.Hirshfeld surface analysis of 1,2,4-triazolium mesylate.
a) Hirshfeld surface displaying contact distances shorter than sum of van der Waal (vdW) radii in red and interactions equal or longer than sum of vdW radii from white to blue. b) finger print map of Hirshfeld surface for interactions between internal oxygen and hydrogen atoms with external hydrogen and oxygen atoms respectively (colored).

Conclusions

1. 1,2,4-triazolium based organic salts were tested as PCMs.
2. Among studied salts the optimum thermal properties were obtained for 1,2,4-triazolium mesylate: T_m=137 °C, $\triangle H_f$ = 140 J.g^{-1}.
3. Hydrogen bonding network in [1,2,4-TAM][CH_3SO_3] mainly drives the high heat of fusion.

Literature

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Acknowledgment

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