Distinguishing the Glass, Crystal, and Quasi-Liquid Layer in 1-Methylnaphthalene by using Fluorescence Signatures

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Crystalline and vitrified states differ in numerous properties, such as the mechanical behavior, expansivity, thermal conductivity, luminescence, X-ray and neutron diffraction, and chemical reactivity. The decision on whether any given compound will crystallize or vitrify when cooled down from its liquid phase depends on the time allowed for the solidification [1]. The speciation of polycyclic aromatic hydrocarbons (PAHs) plays a crucial role in their fate in the atmosphere, fresh and sea water, soil, ice, and also the interstellar space. [2]

Besides other techniques, the fluorescence of polycyclic aromatic hydrocarbons (PAHs) facilitates distinguishing their speciation. [3] The fluorescence of crystalline 1-methylnaphthalene (MeNp) is monomer-like, while liquid and glass exhibit excimeric emissions. The temperature dependence of the fluorescence emission and excitation spectra in the range between 77 K and 295 K provide comprensive information on the state of 1-methylnaphthalene. The glass, formed by abrupt quenching in liquid nitrogen or methane, devitrifies at (155 ± 5) K, allowing the liquid to undergo cold crystallization at around 170 K. In 1-methylnaphthalene crystals, an excimeric emission appears at approximately 40 K below the melting point, a process we ascribe to the formation of dimers due to surface premelting; such a quasi-liquid layer exists at the surface well below the freezing point, remaining uncrystallized. The premelted layer is clearly distinguishable from the bulk glass via fluorescence spectroscopy, which facilitates state identification. With this knowledge, MeNp may find use as a simple molecular probe at sub-zero conditions to study the speciation and aggregation in different environments; alternatively, it may render MeNp applicable as a molecular switch.

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2. Knopf, D.A., P.A. Alpert, and B. Wang, *The Role of Organic Aerosol in Atmospheric Ice Nucleation: A Review.* ACS Earth and Space Chemistry, 2018. **2**(3): p. 168-202.
3. Zezula, J., et al., *Distinguishing the glass, crystal, and quasi-liquid layer in 1-methylnaphthalene by using fluorescence signatures.* Journal of Luminescence, 2023. **261**.