MS29 Molecular interactions in crystal packing and molecular assemblies

Chairs: Kari Rissanen, Doris Braun

MS29-P1 Molecular Structure, FT-IR and UV-Vis Spectra, NBO, NPA and Fukui Function Analysis of (E)-2-((4-bromophenylimino)methyl) -3-methoxyphenol

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A new o-hydroxy Schiff base of the title compound was isolated and investigated by experimental (X-ray diffraction, FT-IR, UV–Vis) and theoretical (DFT, FT-IR, UV–Vis) methodologies.The experimental investigations of the compound indicated that the molecule seems to be in enol form and this is also supported by the results obtained from the theoretical density functional theory (DFT)'s calculations, performed both for the enol and keto tautomers of the title compound. Stability of the molecule arises from hyper conjugative interactions, charge delocalization and hydrogen bond interactions and these have been analyzed using natural bond orbital (NBO) analysis. Additionally, frontier molecular orbitals (HOMO, LUMO), molecular electrostatic potential (MEP), Mulliken population method, Natural Population Analysis (NPA) and Fukui function analysis have been studied.

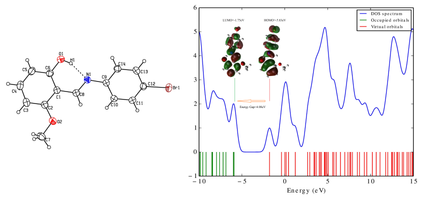

Figure 1. Molecular structure and calculated TDOS spectrum of the title compound.

Keywords: X-ray Diffraction Method, Natural Bond Analysis (NBO), Natural Population Analysis (NPA), Fukui Function Analysis

MS29-P2 Spontaneous reduction of polydispersity and self-healing colloidal crystals

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Crystallization is often suppressed by the presence of point defects due to larger atoms or impurity particles. Surprisingly, colloidal pNIPAM hydrogels can overcome this limitation: A small number of large microgels can spontaneously deswell to fit in the crystal lattice of smaller but otherwise identical microgels, thus avoiding the occurrence of point defects [1]. We find this unique reduction of polydispersity and particle deswelling to be due to an osmotic pressure difference between the inside and the outside of the microgels [2]. Although pNIPAM is an uncharged polymer, pNIPAM microgels carry charged groups, remaining from particle synthesis, on their surface, and most of the corresponding counterions are bound to the particle. An osmotic pressure difference between inside and outside of a microgel builds up when the counterion clouds of neighboring particles overlap. With increasing concentration, this pressure difference exceeds the bulk modulus of the large microgels and makes them deswell, enabling crystallization without point defects. Compared to hard colloidal particles, this particle deswelling mechanism fundamentally changes the role of polydispersity in pNIPAM suspensions and possibly other soft polymer particles. We find the freezing point of bidisperse pNIPAM suspensions to be determined by particle deswelling: A reduction of polydispersity by deswelling of the large particles in the bidisperse suspensions is required for crystallization. Compared to monodisperse suspensions, this causes the freezing point to shift to higher concentrations.

[1] A. St. J. Iyer and L. A. Lyon, Angew. Int. Ed. 48: 4562-4566 (2009).

[2] A. Scotti, U. Gasser, E.S. Herman, M. Pelaez-Fernandez, Jun Han, A. Menzel, L.A. Lyon, and A. Fernandez-Nieves, accepted for publication in PNAS (2016).

Keywords: crystallization, microgels, osmotic pressure, SANS, SAXS