Molecular Origins of Mesoscale Ordering in a Metalloamphiphile Phase

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Controlling the assembly of soft and deformable molecular aggregates into mesoscale structures is essential for understanding and developing a broad range of processes including rare earths extraction and cleaning of water, as well as for developing materials with unique properties.

We studied a metalloamphiphile-oil solution that organize on multiple length scales, where molecules associate into aggregates and aggregates flocculate into meso-ordered phases. By integrating the synchrotron small- and wide-angle X-ray scattering experiment (SWAXS) and large-scale atomistic molecular dynamics simulations, we investigated the structural features of the aggregates. Furthermore, the interactions which drive the aggregate flocculation are also revealed. It is for the first time quantitatively calculated from atomistic simulations that the dipolar interactions ($-0.6 \pm 1.5\ k_BT$) between neighbor aggregates play a dominant role in the effective inter-aggregate interactions ($-0.7\ k_BT$). This calculated effective interactions approximately agree with the experimental value of $-1.3\ k_BT$ obtained by fitting the experimental SAXS data with the Baxter sticky hard sphere model. Our results highlight the importance of individual intermolecular interactions in driving mesoscale ordering.

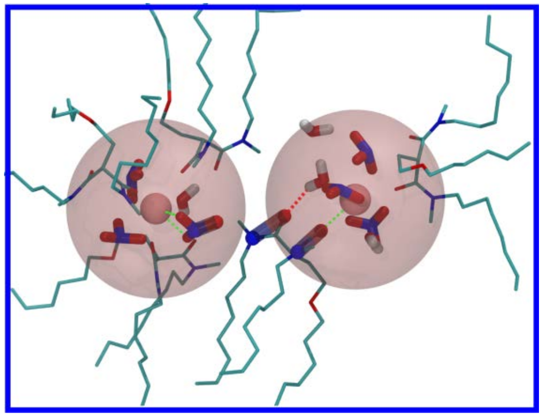

Figure: Snapshots illustrating the interactions between Eu^{3+} centered reverse micelles. The hydrophilic core regions are highlighted by the red shadow areas. The dipolar interactions are indicated by the sticks with blue/red referring to positive/negative atoms, respectively.

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