

Towards 2D Spectroscopy of Molecular Aggregate Formation

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The self-assembly dynamics of tubular J-aggregates were investigated by combining time-resolved spectroscopy and microfluidics. By projecting the aggregate formation process into space, this novel lab-on-a-chip approach could reveal intermediate aggregation species.

In recent decades, self-assembly has excelled as a versatile and powerful technique for the fabrication of nanoscale or supramolecular structures employed in various fields of science. [1] The striking advantage of such approach is that once a detailed understanding of the assembly dynamics was obtained, the fabrication of such structures does not require human intervention and yields reliable results. One class of self-assembling materials that has attracted special interest during past years are chemical derivatives of cyanine dyes, e.g. the C8S3 molecule, that form tubular J-aggregates in aqueous solution resembling the structure of highly efficient light harvesting systems. [2] Despite the efforts of molecular dynamics simulations and sophisticated microscopy experiments, surprisingly little is known on how the aggregation develops in time on a molecular level.

In this contribution we present a novel lab-on-a-chip approach to experimentally resolve the aggregation process by combining time-resolved spectroscopy with microfluidics. The latter projects the reaction coordinate into space such that a self-assembly process is stretched along the spatial coordinate by mixing the two parent reactants in a thin channel. [3] Herewith, different stages of the assembly process become accessible for spectroscopy by probing at different channel position. Intermediate aggregation species can now be resolved using the temporal spectral evolution as a contrast parameter. Applying this technique to our model system C8S3 has proven the existence of intermediate aggregation species. Ultimately, 2D correlations spectroscopy combined with MD and quantum-mechanical simulations will provide more insight into the molecular structure of the transitional reaction stages.

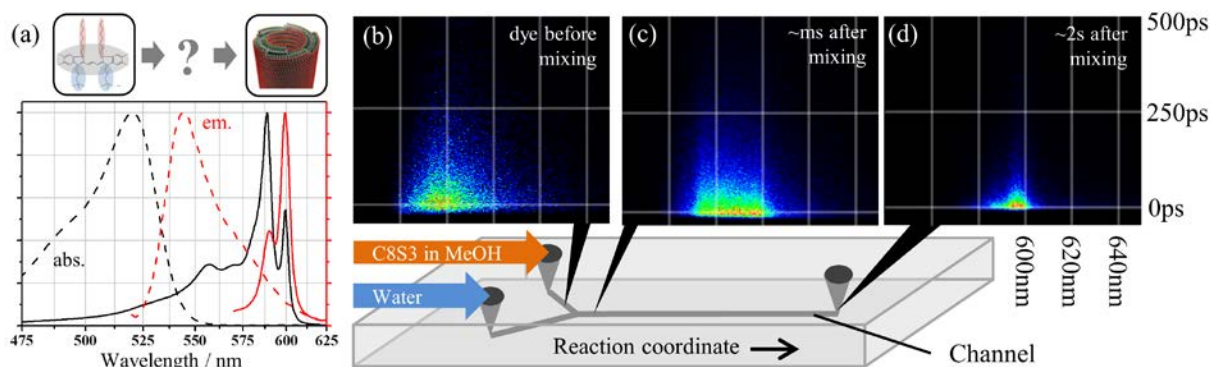


Fig.1 (a) Linear absorption and fluorescence spectra of C8S3 monomers (dashed lines) and aggregates (solid lines). The upper panel schematically shows the chemical structure of C8S3 and tubular structure of the aggregates adapted from [2]. (b), (c) and (d) depict fluorescence decay maps recorded at different reaction coordinates (vertical coordinate is time, the horizontal coordinate is wavelength). As evident from panel (c), the observed emission spectrum cannot be explained with only contributions from single molecules and aggregates, which proves the existence of an intermediate aggregation species.

[1] G. M. Whitesides and B. Grzybowski, *Science* **295**, 2418 (2002).

[2] D. M. Eisele *et al.*, *Nature Chemistry* **4**, 655 (2012).

[3] M. V. Barich and A. T. Krummel, *Anal. Chem.* **85**, 10000 (2013).