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Macroscopic Phase Separation Kinetics of $TPPS_4$ J-aggregate Solutions Analyzed with Confocal Microscopy

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The temporal feature of Confocal Laser Scanning Microscopy (CLSM) has been employed to investigate the structure and kinetics of aqueous solutions of meso-tetra (4-sulphonatophenyl) porphine aggregates. $TPPS_4$ self-associate at acidic pH conditions into molecularly assembled nanorods with a length of ~1 μm [2]. There are indications that these aggregates assemble into larger macrostructures. We have confirmed the existence of such larger macrostructures with CLSM and studied their structural details and kinetic behavior.

Several CLSM experiments on these J-aggregates have been performed to elucidate both kinetic and morphological information. Approximately 10 μl of $TPPS_4$ sample has been placed in a 10 μm deep flat-well quartz cell and placed on a microscope stage for about 15 hours to allow any shear-induced motion to cease. Two three-dimensional section series, each comprised of a stack of 35 two-dimensional images (section slices), are measured. In another experiment, a single image slice has been scanned every 60 seconds for 20 minutes, compiling a composite picture of the kinetics of this aggregation process.

$TPPS_4$ solutions have been brought out-of-equilibrium by the addition of a 1 M solution of HCl, conditions under which we have confirmed the formation of macro-assemblies. $TPPS_4$ has been chosen because of the fluorescent properties of the porphyrine molecule, which allows investigation of the structures formed in or from solution. The fluorescence changes of this kinetic aggregation process have been observed using a CLSM equipped with an Argon/Krypton Laser. The shape and size of the macro-assemblies have been observed using the time-lapse feature of the CLSM at a wavelength of 568 ηm. The emission spectrum for $TPPS_4$ has been determined to be > 650 ηm so a 590 ηm long pass filter has been used to enhance contrast of the aggregate formation [1]. The time evolution and morphological structure of the aggregate formation process vary with the volume fraction of the added $TPPS_4$. Over time these aggregated structures accrete and form a somewhat rigid network before they reach equilibrium. This fractal macro-assembly process closely resembles Diffusion Limited Cluster Aggregation (DLCA) process, but further investigation of this phenomenon has to be conducted before such conclusions can be asserted.

References

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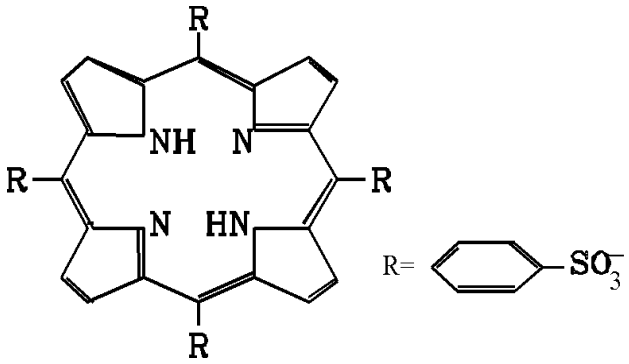

Fig.1 The structure of meso-tetra (4-sulphonatophenyl) porphine ($TPPS_4$) Ref [4].

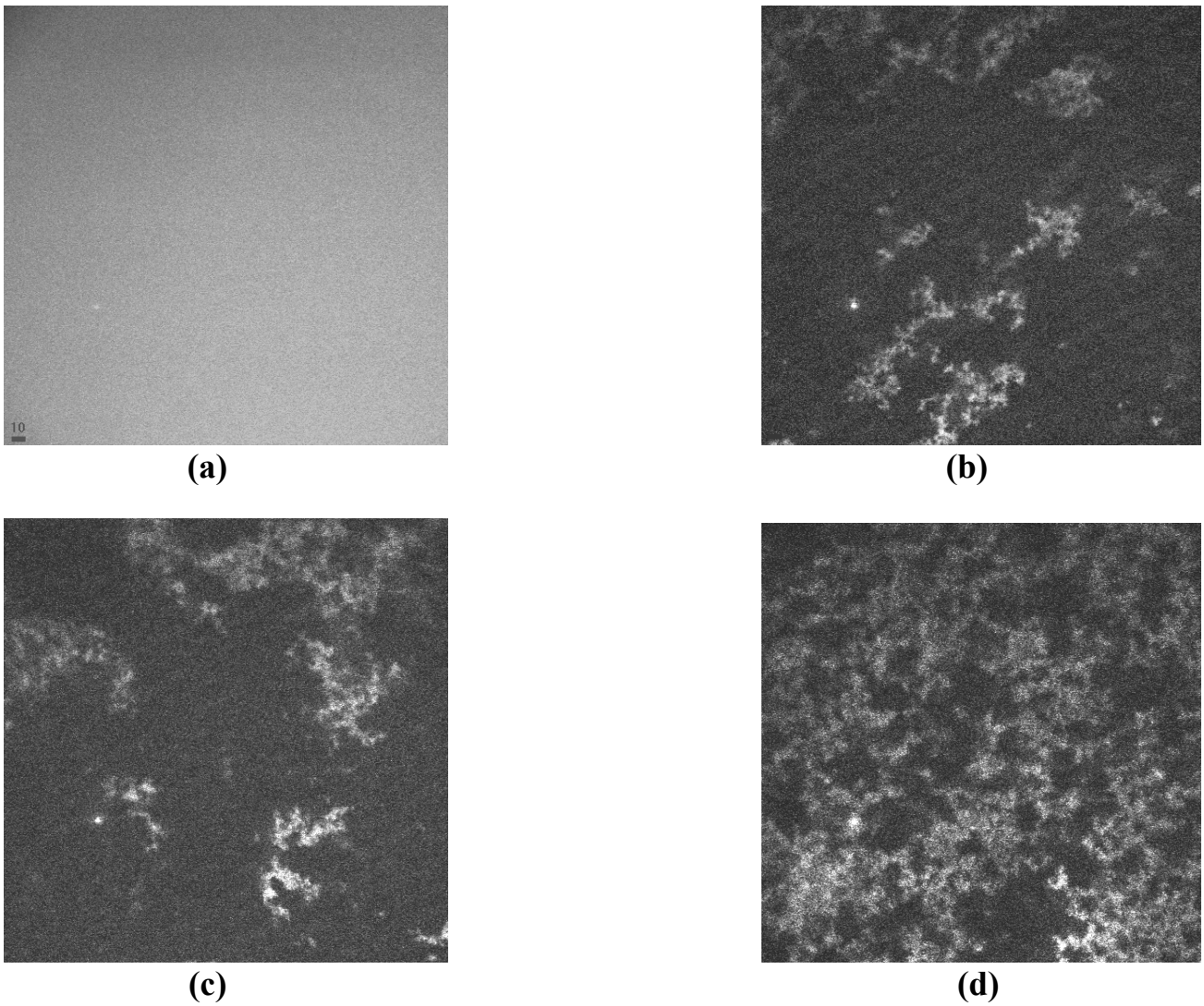

Fig.2 (a)$TPPS_4$ solution (250 μM) in phosphate buffer. (b) $TPPS_4$ solution (125 μM) after addition of HCL (1 M). (c)$TPPS_4$ solution (230 μM) after addition of HCL (1 M). (d) $TPPS_4$ solution (750 μM) after addition of HCL (1 M). Scale bar for above 512 x 512 μm images is 10 microns.

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