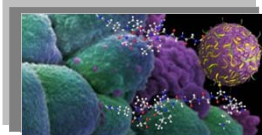


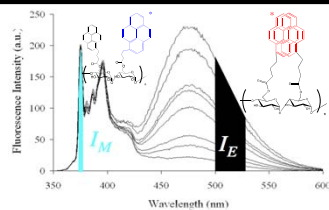
## Introduction

The numerous functional groups of Starch Nanoparticles (SNPs) allow for their chemical modification, and in turn, the adjustment of their properties. Of particular interest is the hydrophobic modification of SNPs that would turn them into amphiphilic particles. This study aims to characterize how these hydrophobic modifications affect the behavior of the modified SNPs in aqueous solution. To this end,



transmission electron microscopy (TEM) and fluorescence were employed to characterize the internal dynamics and morphology of the hydrophobically modified SNPs.

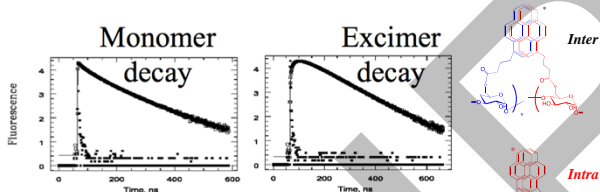
## Steady-State Fluorescence Spectroscopy



$$\frac{I_E}{I_M} = Kk_d[Py]_{exc}$$

$$k_d = 4\pi N_A(D_D + D_P)\sigma$$

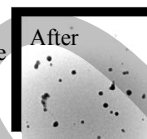
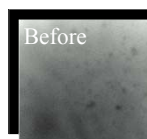
## Time-Resolved Fluorescence Spectroscopy



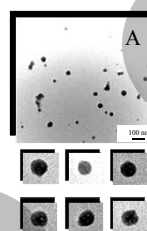
Monomer decays were acquired at 375 nm, and excimer decays were acquired at 510 nm.  $\langle k \rangle$  ( $\mu s^{-1}$ ),  $f_{agg}$ ,  $f_{free}$ , and  $f_{diff}$  are determined from the life-time measurements.

## Staining with Ruthenium Tetroxide (RuO<sub>4</sub>)

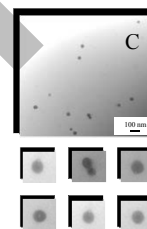
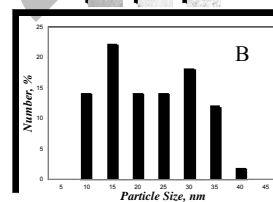
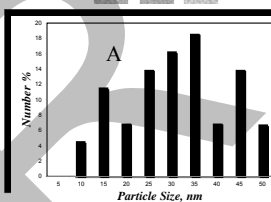
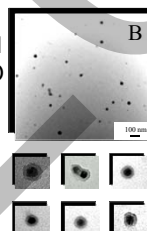
- RuO<sub>4</sub> (0.5 % aqueous solution)
- Stained in a petri dish (fume hood)
- The best staining time is 45 s
- Used within 2-12 hours
- Protective equipment was worn at all time
- Waste was processed separately



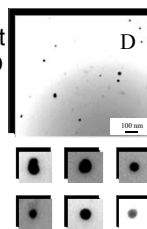
## Morphology and Size Distribution from TEM



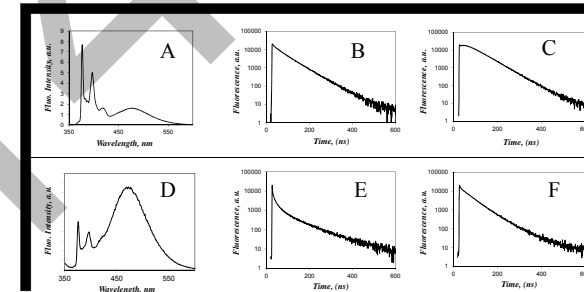
Pyrene-labeled SNPs in DMSO (A, left) and water (B, right)



Non-fluorescent SNPs in DMSO (C, left) and water (D, right)



## Results from SS & TR Fluorescence



Figures above present the steady-state fluorescence spectra ( $\lambda_{ex}=344$  nm) of pyrene-labeled SNPs in (A) DMSO and (B) water ( $\lambda_{ex}=344$  nm,  $\lambda_{em}=375$  nm) and time-resolved fluorescence decays of the pyrene monomer in (C) DMSO and (D) water and of the pyrene excimer in (E) DMSO and (F) water.

| Solvent | $\eta@25^\circ C$<br>mPa·s | $I_E/I_M$ | $\langle k \rangle$ , $\mu s^{-1}$ | $f_{diff}\%$ | $f_{free}\%$ | $f_{agg}\%$ |
|---------|----------------------------|-----------|------------------------------------|--------------|--------------|-------------|
| DMSO    | 1.99                       | 0.68      | 9.80                               | 79.70        | 2.20         | 18.10       |
| Water   | 0.89                       | 5.65      | 52.10                              | 5.00         | 0            | 95.00       |

## Summary

- In water, 95% of the pyrene excimer originated from the direct excitation of pre-associated pyrene aggregate
- Only 5% of the excimer was formed diffusion in water.
- The average quenching rate constant  $\langle k \rangle$  is 5 times faster in water than in DMSO
- The particle size in DMSO is 30 nm, which is 10 nm larger than in water 20 nm
- The core-shell structure was only observed by TEM for the hydrophobically modified pyrene-labeled SNPs

## Reference

Zachariasse, K.; Kühnle, *Zeit. Phys. Chem.* **1976**, *101*, 267-276.  
Winnik, M. A.; Redpath, T.; Richards, D. H. *Macromolecules* **1980**, *13*, 328-335.