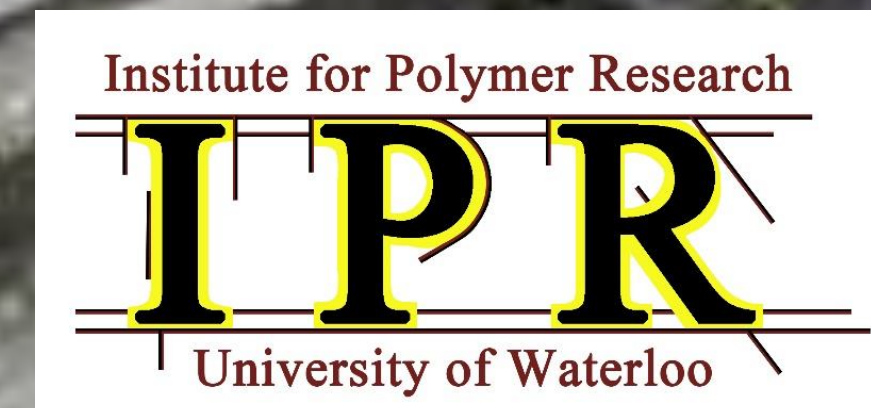


# Characterization of Hydrophobically Modified Starch NanoParticles

## by Pyrene Fluorescence

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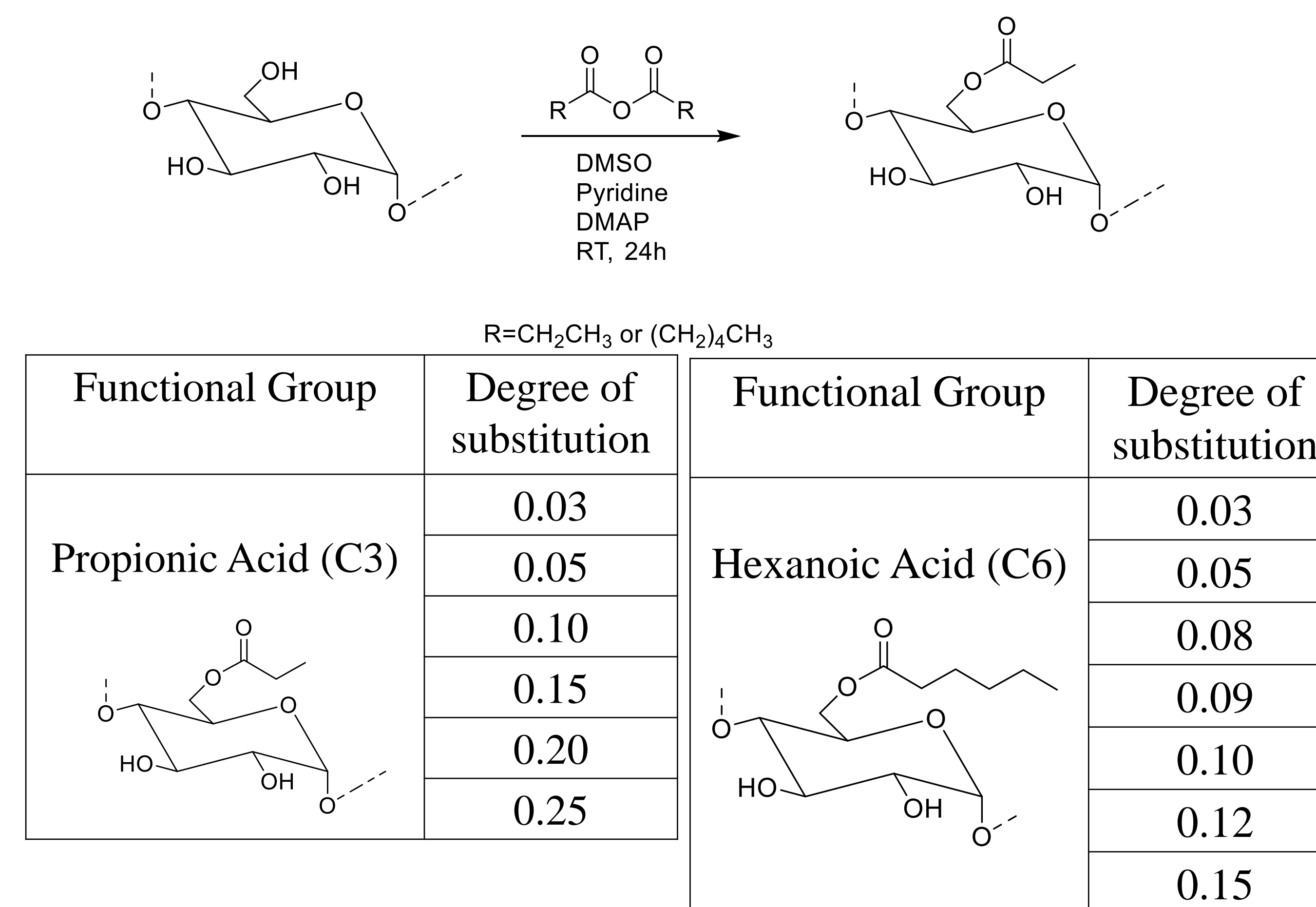
### Abstract

Starch NanoParticles (SNPs) modified with hexanoic anhydride were examined by the technique of fluorescence spectroscopy using pyrene in order to verify the presence of hydrophobic microdomains upon dispersion in water and to examine their level of hydrophobicity. Fluorescence parameters such as  $\tau_0$ ,  $k_q$ ,  $I_1/I_3$ ,  $K_B$ , and pyrene loading capacity were obtained to quantify the level of the hydrophobicity of the SNPs. An increase in  $\tau_0$  and a decrease in  $k_q$  and  $I_1/I_3$  with increasing degree of substitution (DS) of propionic/hexanoic anhydride demonstrated that the environment provided by the modified SNPs was more viscous and less polar. Increase in  $K_B$  and loading capacity with increasing DS indicated that the modified SNPs with a higher DS had increased interactions with the hydrophobic molecules thereby indicating their potential as carriers of hydrophobic compounds. The delay of binding of pyrene to HM-SNPs was observed at high concentration of HM-SNPs which indicates the reduction of the surface area due to the aggregation. The diameters of HM-SNP at different concentrations were estimated with the model and demonstrated with a diameter obtained from Dynamic Light Scattering (DLS) measurement.

### Introduction

Starch NanoParticles (SNPs) were modified with different degrees of substitution (DS) of hexanoic anhydride in order to change their amphiphilic character. This modification led to the formation of hydrophobic microdomains upon dispersion of the modified SNPs in water. The presence of hydrophobic microdomains allowed SNPs to uptake hydrophobic molecules such as pyrene. As the hydrophobicity of SNPs increased, the interactions with pyrene were expected to increase which could be demonstrated monitoring the loading capacity and binding constant ( $K_B$ ) of pyrene to the modified SNPs. Pyrene has distinguishable fluorescence properties that can be applied to describe the level of hydrophobicity. The hydrophobicity of the modified SNPs were examined with these five fluorescence parameters.

### Synthesis



### Results and discussion

#### Quenching Study

$$\text{Stern Volmer Equation } \frac{I_0}{I} = \frac{\tau_0}{\tau} = \tau_0 k_q [\text{Quencher}] + 1$$

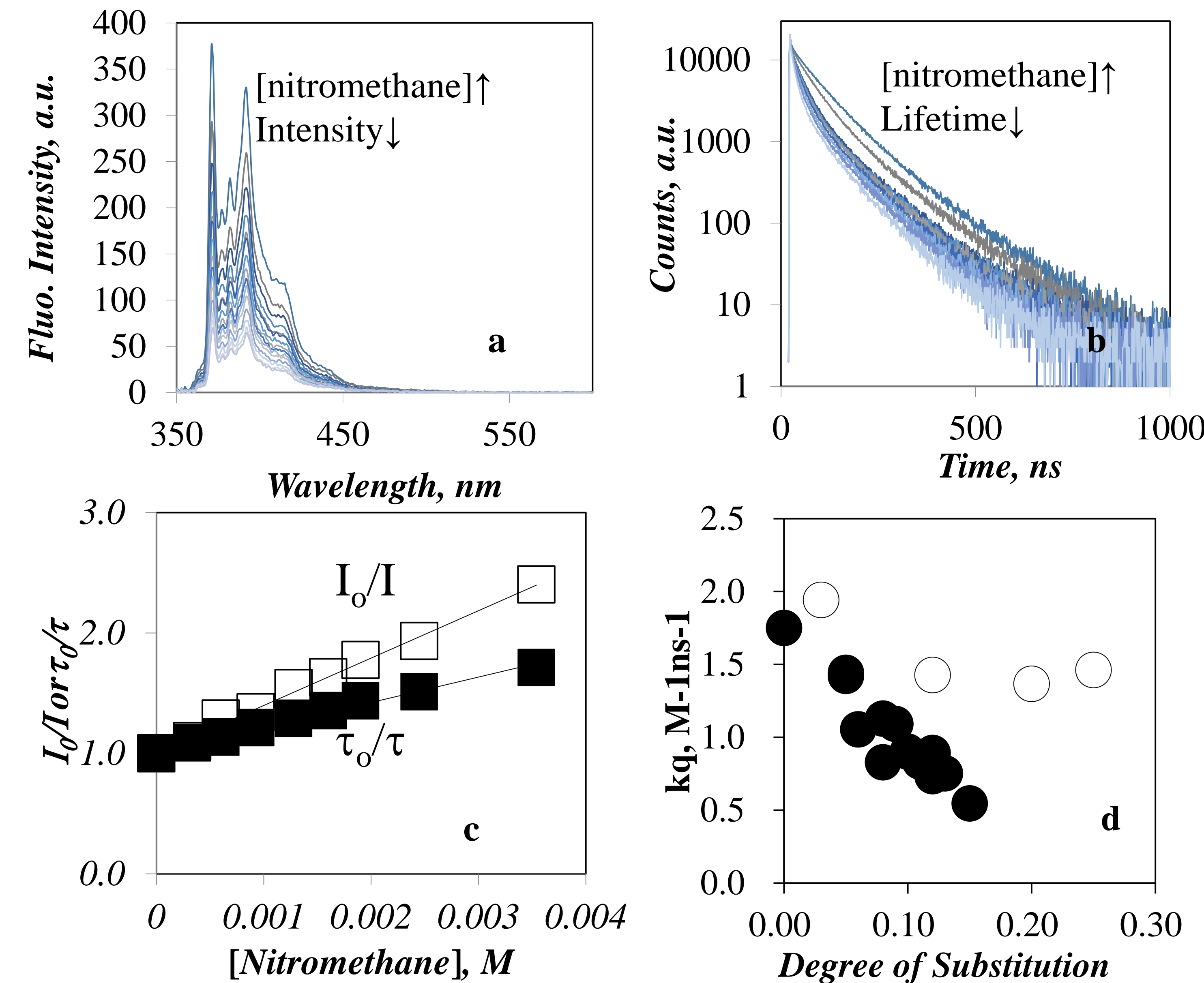


Figure 1. a) Fluorescence spectra and b) fluorescence decays of pyrene loaded HM-SNPs at different [nitromethane]. c) Stern-Volmer plot. d) Bimolecular rate constant for quenching of pyrene by nitromethane as a function of DS of hexanoic acid

### Binding and Loading Capacity

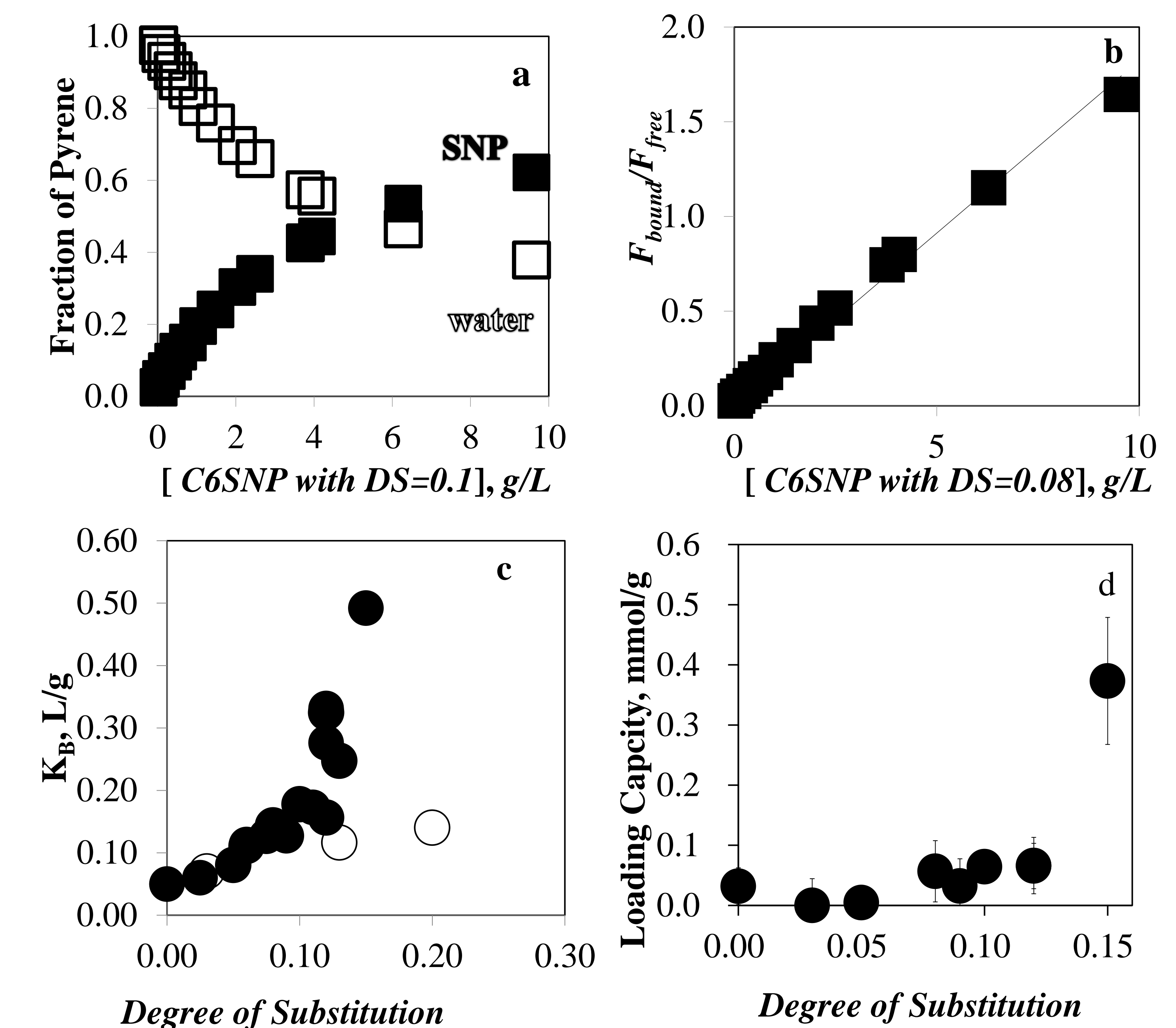
$$\text{Binding constant } K_B = \frac{F_{\text{Pybound}}}{F_{\text{Pywater}} [\text{SNP}]}$$


Figure 3. a) Change in fraction of pyrene in water and bound to HM-SNP b) Plot of the ratio of pyrene concentration in water over pyrene bound to HM-SNP as a function of [HM-SNP] c) Change in binding constant ( $K_B$ ) and d) Loading capacity of pyrene as a function of DS

#### Aggregation of HM-SNP

Pyrene binds to the surface of HM-SNP. HM-SNPs begins to aggregate at high concentration which results in the delay of binding of pyrene to HM-SNPs

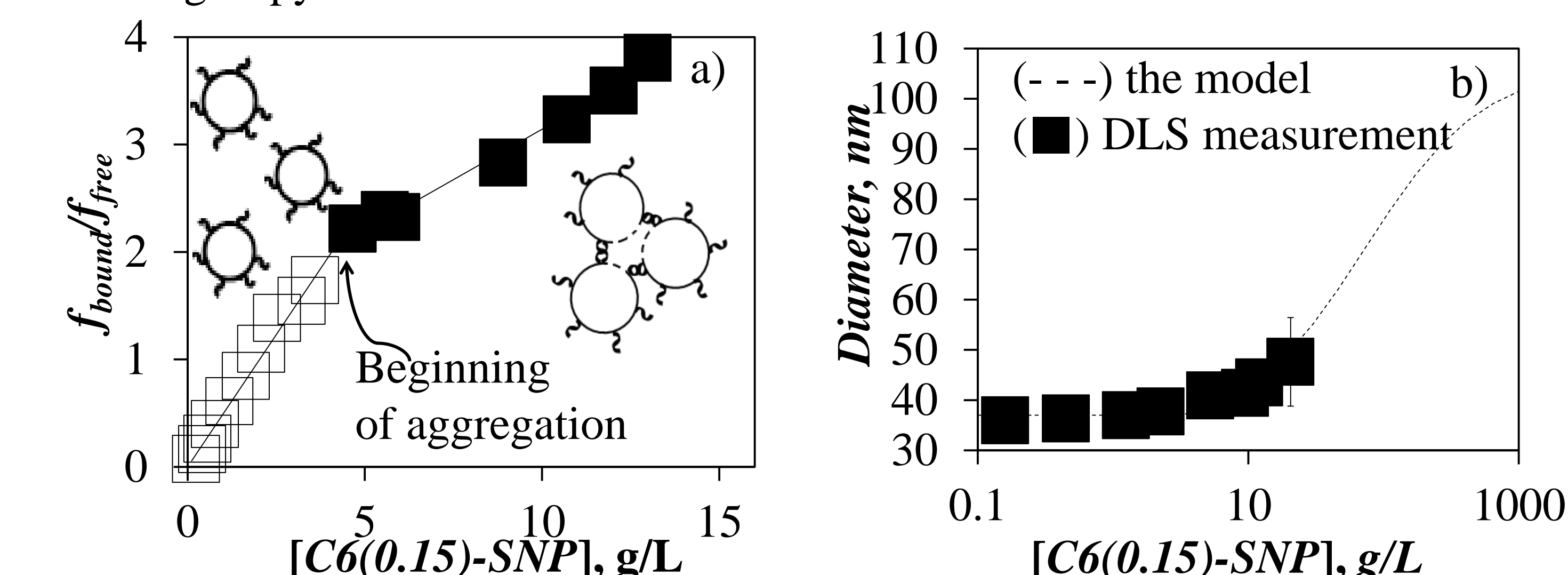
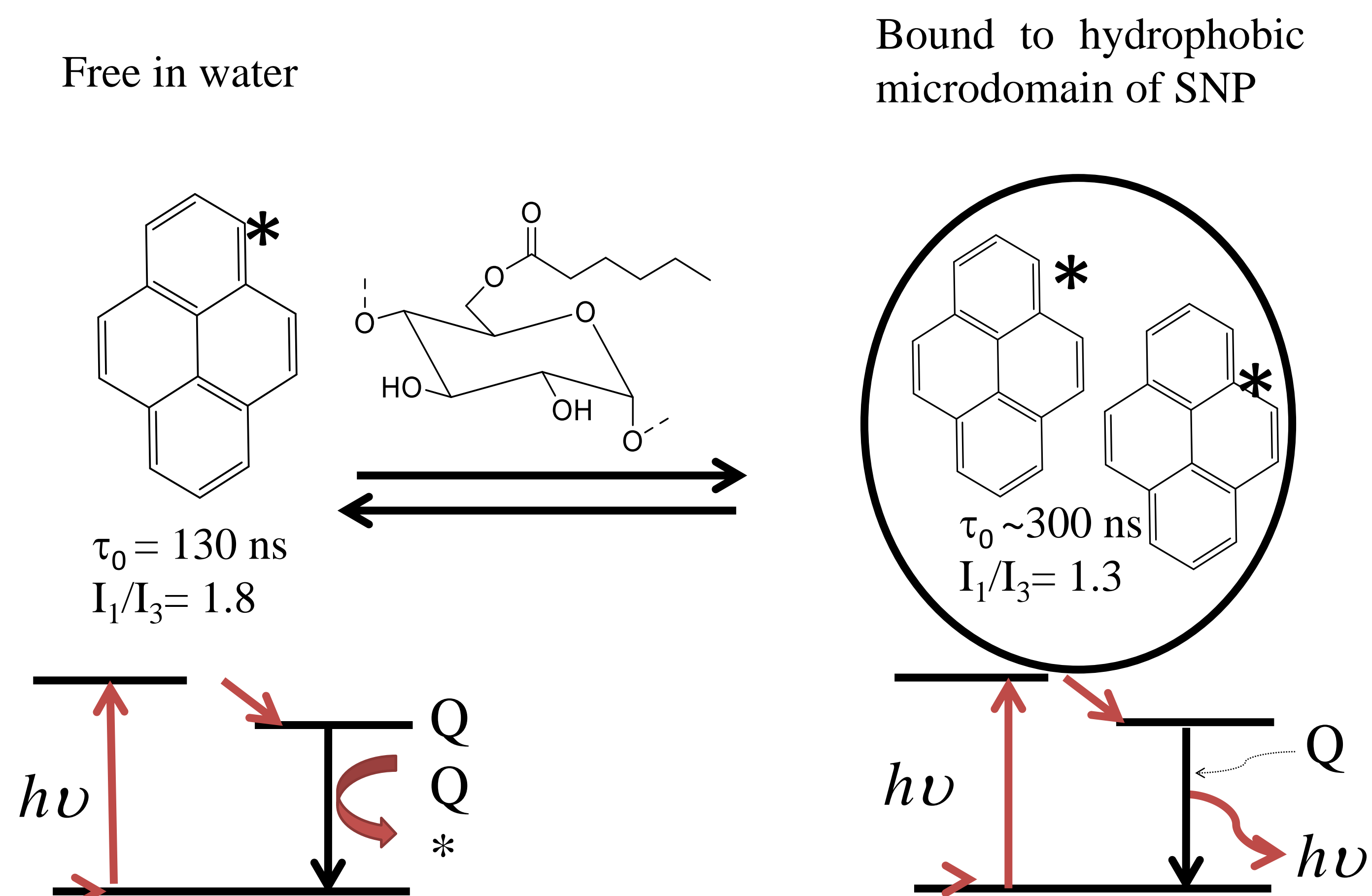


Figure 3. Plot of (a)  $f_{\text{bound}}/f_{\text{free}}$  and (b) the hydrodynamic diameter predicted from Equation 3 (---) and measured by DLS (■) as a function of C6(0.15)-SNP concentration.

#### Acknowledgements

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Scheme 1. Differences in pyrene emission in the absence/ presence of hydrophobic microdomains