

# Solution-State NMR Studies of Polystyrene Nanoparticle-Small Molecule Interactions

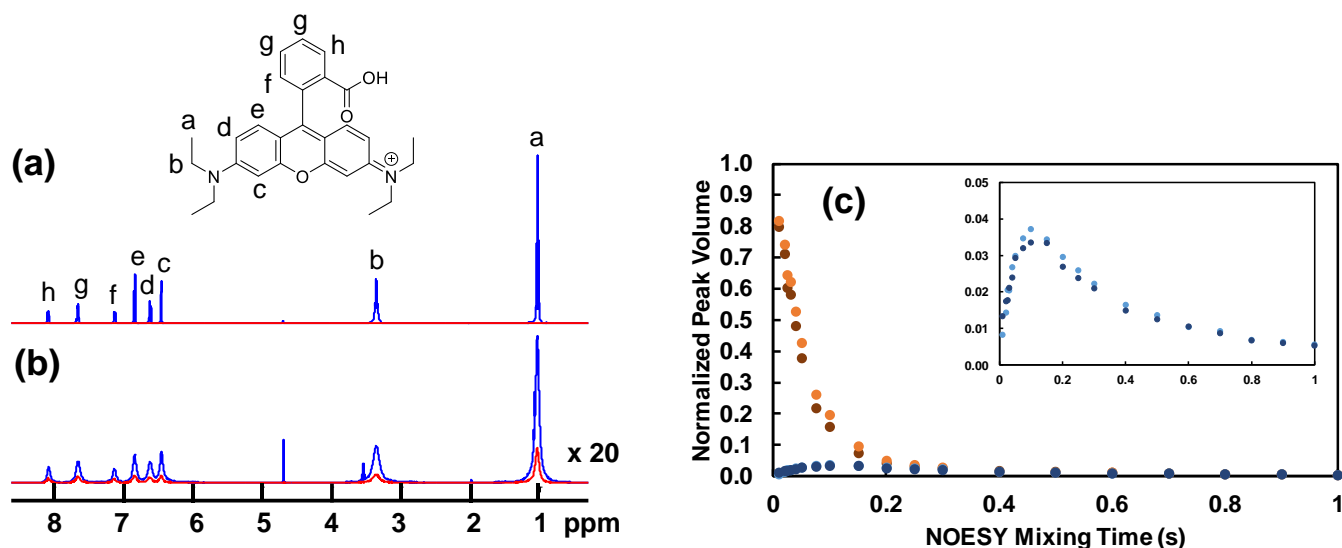
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Interactions between nanoparticles and small molecules in solution are important in a variety of fields. Understanding nanoparticle surface interactions is important in nanoparticle catalysis,<sup>1</sup> interactions between dyes and nanoparticle surfaces are relevant to designing dual-use (for example fluorescence and MRI) imaging agents,<sup>2</sup> and inorganic nanoparticles are often coated with peptides in order to make them more biocompatible.<sup>3</sup>

Due to the large size of nanoparticles and their corresponding long rotational correlation times, solid-state NMR is usually the method of choice for characterizing the structure of ligands on the surface of nanoparticles. In solution, strongly-bound ligands will also have the same long rotational correlation times as the nanoparticle itself, making them often invisible in solution-state NMR. However, several ligand-detected NMR techniques are available for obtaining information about nanoparticle-ligand binding in solution.<sup>4</sup> These solution-state NMR measurements complement the solid-state NMR work by giving information about dynamics, ligand exchange, binding constants, and structure in solution.

Here we report on recent work using solution-state NMR techniques, including Saturation-Transfer Difference (STD)-NMR, pulsed field gradient experiments to measure diffusion coefficients, relaxation time measurements, and NOESY experiments to characterize the binding between small molecules, such as amino acids and dyes, and the surface of polystyrene nanoparticles. This work may lead to methods for screening biologically-relevant molecules that interact with nano-scale plastic pollutants.<sup>5</sup>



**Figure 1.** Fluorescent dye rhodamine B interacting with 40-nm polystyrene nanoparticles. (a) Structure of rhodamine B with proton NMR peak assignments from reference 6. In red is the control STD difference spectrum with a saturation time of 1.5 seconds for a sample of rhodamine B in the absence of nanoparticles. (b) STD reference spectrum (blue) and STD difference spectrum (red) for rhodamine B interacting with 40-nm nanoparticles. The saturation time is 1.5 s. Note that rhodamine peaks experience significant line broadening in the presence of the nanoparticles. (c) NOESY peak volumes as a function of NOESY mixing time for diagonal peaks (orange) and cross peaks (blue) between protons f and h of rhodamine B in the presence of 40-nm nanoparticles. The inset is an expansion of the cross peak intensity, which is indicative of a long rotational correlation time.

## References

- (1) Morales-Leal, F. J.; Rivera de la Rosa, J.; Lucio-Ortiz, C. J.; De Haro-Del Rio, D. A.; Solis Maldonado, C.; Wi, S.; Casabianca, L. B.; Garcia, C. D. *Appl. Catal. B – Environ.* **2019**, *244*, 250-261.
- (2) Song, J. T.; Yang, X. Q.; Zhang, X. S.; Yan, D. M.; Wang, Z. Y.; Zhao, Y. D. *ACS Appl. Mater. Interfaces* **2015**, *7*, 17287-17297.
- (3) Zhan, N.; Palui, G.; Kapur, A.; Palomo, V.; Dawson, P. E.; Mattoussi, H. *J. Am. Chem. Soc.* **2015**, *137*, 16084-16097.
- (4) Hens, Z.; Martins, J. C. *Chem. Mater.* **2013**, *25*, 1211-1221.
- (5) Mattsson, K.; Hansson, L.-A.; Cedervall, T. *Environ. Sci.: Processes Impacts* **2015**, *17*, 1712-1721.
- (6) Serra-Gómez, R.; Tardajos, G.; González-Benito, J.; González-Gaitano, G. *Dyes Pigments* **2012**, *94*, 427-436.