Experimental report

07/09/2022

Proposal: 9-11-2002 **Council:** 4/2020

Title: Using Contrast Matching to Understand the Properties of Perylene Bisimides at different pHs

Research area: Chemistry

This proposal is a new proposal

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Samples: perylene bisimide

Instrument	Requested days	Allocated days	From	To
D11	2	2	14/05/2021	16/05/2021

Abstract:

We have been examining perylene bisimides as potential organic electronic materials. These materials are interesting due to their high molar absorptivity, their ability to self-assemble and form different aggregates depending on environment. These structures and their behaviours, such as conductivity and UV-vis absorption, are highly dependent on the pH the structures are formed at. We plan to use contrast matching and selectively deuterated analogue of the same perylene bisimide to investigate how the molecules pack into the different structures to hopefully explain the differences in properties of the different aggregates.

Experiment Number: 9-11-2002

Experiment Title: Using Contrast Matching to Understand the Properties of Perylene Bisimides at different pHs has no experimental report

Abstract Perylene bisimides (PBIs) are of great interest due to their electronic properties. When irradiated with the right wavelength of light they become conductive due to the formation of a radical anion. This conductive behaviour means that these materials can be used in devices such as transistors and solar cells. We had found that the aggregate greatly effects the behaviour of the materials, but we do not know how the individual molecules are packing into the aggregates. Therefore we carried out some contrast matching SANS with different deuterated molecules to find out more.

Introduction We have been examining perylene bisimides (PBIs) as potential organic electronic materials. These materials are interesting due to their high molar absorptivity, their ability to self-assemble and form different aggregates depending on environment. They accept an electron into their core and to form photo, chemical and electrochemical reduced species, which makes them suitable as semi-conductors. The radical can be analysed by UV-vis absorption spectroscopy, electrochemistry and by EPR spectroscopy to quantify how much radical anion is present. We have carried out a lot of research focusing on these materials, and we have shown that the pH is hugely important in the behavior of the material. Although the pH does not affect the HOMO/LUMO of the material, it does however affect the amount of radical that is stable when the PBI is self-assembled. Therefore, the aggregation type is very important when designing the material for use in organic electronic devices. At pH 10 these molecules form little or no structure However, at around pH 8 we find that these PBI molecules self-assemble in water via pi-pi stack in solution to form worm-like micelles which fit a flexible elliptical cylinder with a power law model as seen in previous SANS experiments. Upon lowering the pH again to 3, further self-assembly occurring and the structures elongate and entangle forming a hydrogel network. These gels fit again to a flexible elliptical cylinder with a power law model, but with differing parameters. At the different pHs despite being the same molecule all have drastically different properties. One of the biggest differences is the conductivity values, with pH 8 giving the best conductivity and pH 10 giving the worst. We would expect the data to be more similar as the HOMO/LUMO has not changed, they fit to the same model, so why are they so different? This is a key question that needs answering.

Experimental In this experiment, we collected data at a Q range of 6 10-4 to 0.6 Å-1 to be able to understand the primary structures (which we fitted to a flexible cylinder, hollow cylinder, or elliptical cylinder model as appropriate) and the network (which was generally captured by a power law in combination with the above models). Samples were collected in 2 mm pathlength quartz cuvettes. Data was collected at multiple Q ranges, at 1m, 8 and 30m. We looked at 3 different pHs (pDs), 10, 8 and 3. For each of the pHs we collected data for the four different PBI-A analogues. We then collected the scattering during gelation by slowly lowering the pH, by the addition of glucono- ∂ -lactone, from pH 10 to pH 4 over 8 hours.

Results Below is some example data collected. All the data collected worked well and had varying degrees of differences at the different pHs and different degrees of protonation. Data below shows the scattering of the same molecule with varying amounts of deuteration. The fully protonated molecule (green) shows the fully scattering profile. The blue data is with the conjugated core deuterated which has a similar scattering profile to the fully protonated, meaning the scattering is coming from the amino acid part of the structures. The red data is with the amino acids deuterated, meaning the scattering is from the core, the profile here looks different to the other scattering profiles, which gives us some indication to how the fibres are forming. More data and modelling need to be carried out on all the data sets in order to fully characterize the system.

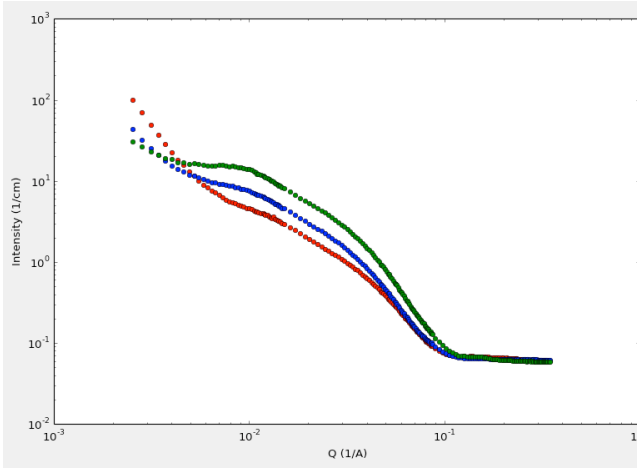

Figure 1. SANS if the different compounds. green all protonated, blue core deuterated and red of the amino acids deuterated