Experimental report

11/09/2019

Proposal: **9-11-1914** **Council:** 10/2018

Title: The stability of colloidal quantumdot ligands in polymer photon multiplier nanocomposites

Research area: Materials

This proposal is a new proposal

Main proposer: **Mike WEIR**

Experimental team: Daniel TOOLAN
Mike WEIR

Local contacts: Ralf SCHWEINS

Samples: PbS-Oleic acid PbS-C18H34O2
PbS-TIPS-Tetracene-carboxylic acid PbS-C40H51Si2CO2H
TIPS-Tetracene C40H52Si2
d-Polystyrene (C8D8)n
d-poly(methylmethacrylate) (C5O2D8)n
PbS-Napthoic acid PbS-C10H7CO2H

Instrument	Requested days	Allocated days	From	To
D11	2	2	08/07/2019	10/07/2019

Abstract:

Photovoltaic (PV) technologies hold the potential to generate low-cost sustainable energy, however, their deployment en masse is currently hampered by their high cost / efficiency ratios. The biggest efficiency loss occurs due to the PVs inability to efficiently harvest the entire solar spectrum, where the absorption of high energy blue light results in energy losses due to thermalization. The photon-multiplier (PM) concept, in which a blue photon is converted into two red photons with efficiency that in principle can reach 100%, is a promising route to reducing such losses. A route for generating PM thin-films that could be easily interfaced with a solar cell involves dispersing singlet fission organic semiconductors and colloidal quantum dots (QD) within a polymer matrix. This experiment aims to gain new insight into the influence of polymer matrices on i) the quality of the QD dispersion and ii) the morphology of the QD ligand envelope. Due to the contrast provided by isotopic labelling (deuteration of the polymer matrix), SANS is an ideal technique to make this measurement.

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The stability of colloidal quantum dot ligands in polymer photon multiplier nanocomposites

Mike WEIR[1], Daniel T. W. TOOLAN[2], Akshay RAO[3], Anthony J. RYAN[2], and Richard A. L. JONES[1]

1. Department of Physics and Astronomy, The University of Sheffield
2. Department of Chemistry, The University of Sheffield
3. Cavendish Laboratory, Cambridge University

Introduction and information.

This experiment took place over 2 days of beamtime on the D11 instrument on 8th-10th July 2019 with local contact Dr. Ralf Schweins. Dr. Dan Toolan and Dr. Mike Weir attended.

The experiment measured lead sulphide-oleic acid (PbS-OA) colloidal quantum dots (QD) with deuterated polystyrene or poly(methyl methacrylate). The samples were measured either as solutions in deuterated toluene, to measure the interactions between the polymers and QD in solution, or as nanocomposites spin-coated onto quartz substrates to measure the state of the QD ligand shells and (to some extent) to confirm the arrangement of the QD within the respective polymer matrices.

The experiment was a technical success in terms of beam stability and sample environment and the overwhelming majority of the available neutron beam time was put to productive use. Local contacting and user support were extremely good. Some short comments about the mounting of quartz substrates are included in the relevant section below.

Due to the progress in their initial characterisation, and time constraints in the reality of the experiment, the functional naphthoic acid and TIPS-tetracene caryboxylic acid liganded QD mentioned in the initial proposal were not measured. This is still of importance and we will be likely to ask for a continuation to carry on to studying these important samples.

Solutions.

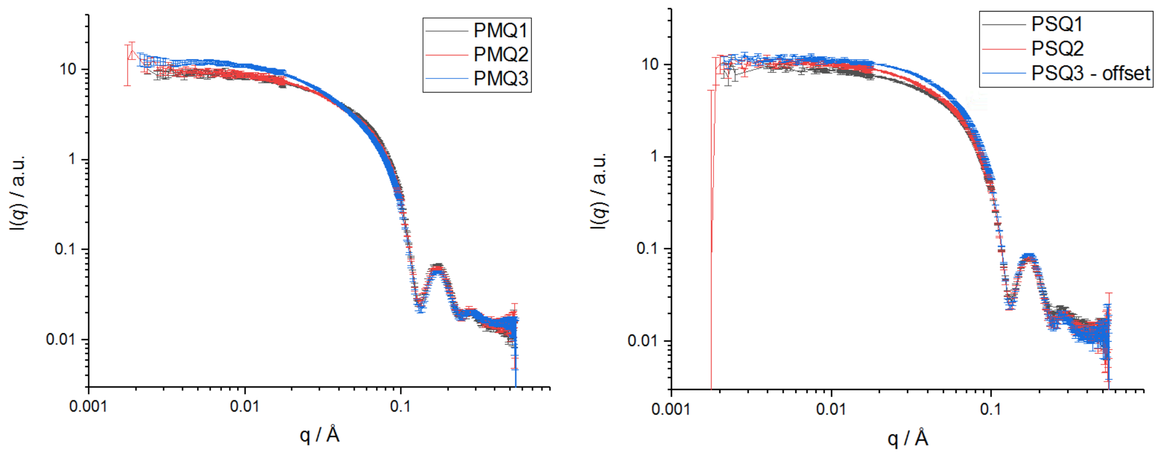

Figure 1. Solution SANS from 20 mg/mL PbS-OA QD with PMMA and PS at various concentrations where 1 = 4 wt%, 2 = 8 wt% and 3 = 16 wt %.

Solution SANS from the polymer-QD solutions in deuterated toluene were highly successful, with the favourable contrast and low size polydispersity of the QD leading to good signal-to-noise and pronounced scattering features. Representative data is shown in Figure 1. While it is too early to conclude full fitting of the data there appears to be little or no effect of adding either polymer to the QD solution and therefore our initial conclusion is that little or no ligand stripping is taking place.

Quartz discs.

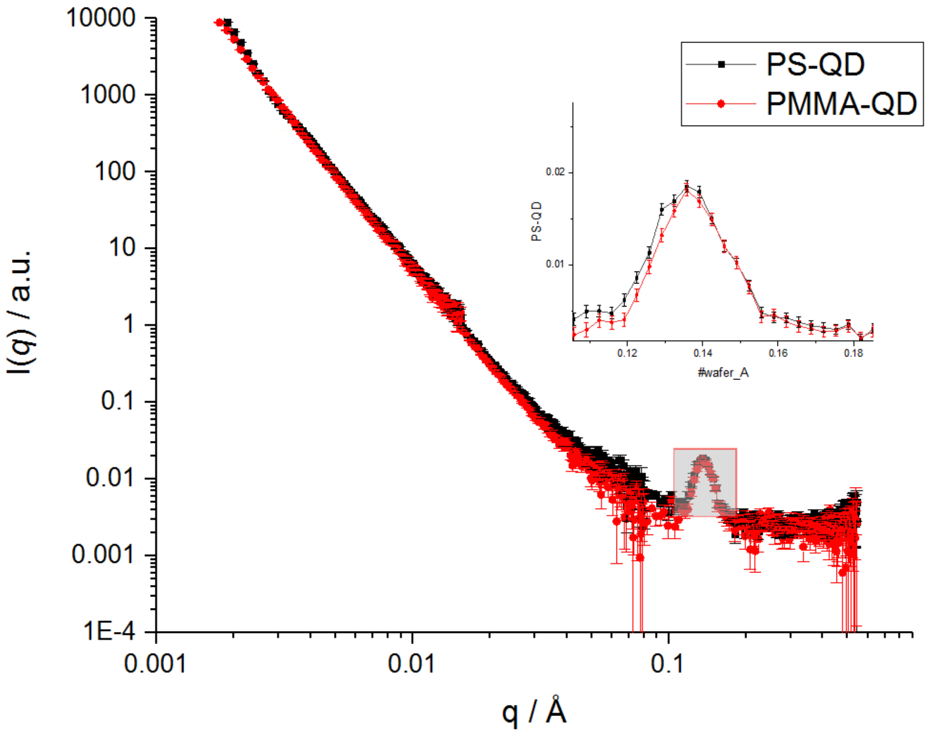

Figure 2. SANS data from stacks of 25 quartz discs with PS-QD or PMMA-QD coated film on each wafer.

Stacks of 25 discs were mounted in custom made holders that were mounted on top of the normal sample changer. They produced sufficient scattering to enable us to determine the QD structure and arrangement. SANS data for some representative samples is shown in Figure 2. Again, it was noted that the contrast scenario and count time were appropriate to resolve the required information. Similar to the solution scattering from Figure 1, however, it was noted that little or no change in the QD structure was observed between PS and PMMA and that our initial conclusion is that little or no ligand stripping had taken place.

During the experiment it was ascertained that a single quartz substrate did not produce sufficient scattering to be used on its own. The purpose of this was to decide whether we could remove the background that appears to arise from stacking several samples, but still measure a signal from the thin film structure.

Conclusion.

This was a successful, technically feasible, and well-supported experiment. The quality of the data is apparent. The lack of a ligand stripping effect in PbS-OA QD with PS and PMMA solutions or nanocomposites is interesting as it suggests the stripping effects may be ligand specific. It is likely that we will ask for a continuation to study PbS-TIPS-tetracene-carboxylic acid quantum dots in similar matrices and also explore more the effect of annealing at elevated temperatures. We have a high degree of confidence that this study will contribute to a good quality publication. One thing worthy of note is that shortly after the beamtime, we published a paper about ligand shell structure in PbS-OA QD using the instruments at the ISIS Pulsed Neutron and Muon source, which helps to consolidate our expertise in this area[1].

1. Weir, M.P., et al., *Ligand Shell Structure in Lead Sulfide–Oleic Acid Colloidal Quantum Dots Revealed by Small-Angle Scattering.* The Journal of Physical Chemistry Letters, 2019. **10**(16): p. 4713-4719.