Research Networking Programmes

Short Visit Grant ☒ or Exchange Visit Grant ☐

(please tick the relevant box)

Scientific Report

The scientific report (WORD or PDF file – maximum of eight A4 pages) should be submitted online within one month of the event. It will be published on the ESF website.

***Proposal Title**:* Determination of number of quantum dots/dye molecules coupled to plasmonic structures

Application Reference N°: 6509

1) Purpose of the visit

To carry out correlation measurements on the Au rings/QD system; to have discussions on the collaborative work to be carried out in the coming months; to carry out tests on selective deposition of J-aggregates.

2) Description of the work carried out during the visit

Held several meetings with Prof. Rakovich and Dr. Melnikau about ongoing collaborative work.

Tested solubility of JC-1, PIC and S-46 J-aggregates in organic solvents. Attempted localised deposition of aggregates of these dyes on glass.

Carried out FLIM and cross-correlation measurements on Au rings/QD system at 488 nm excitation, for different dimensions of Au rings/disks and different positions of QDs inside these rings.

3) Description of the main results obtained

1. Localised deposition of J-aggregates on glass/quartz substrates

Solubility of three J-aggregate samples in organic solvents was tested. In particular, three dyes were used to assemble J-aggregates in water:

- JC-1 (5,5′,6,6′-Tetrachloro-1,1′,3,3′-tetraethyl-imidacarbocyanine iodide)
- PIC (1,1'-diethyl-2,2'-cyanine chloride)

- S-46 (5,6-Dichloro-2-[[5,6-dichloro-1-ethyl-3-(4-sulfobutyl)-benzimidazol-2-ylidene]-propenyl]-1-ethyl-3-(4-sulfobutyl)-benzimidazolium hydroxide, inner salt, sodium salt)

A small volume of acetone or toluene (25% v/v) was added to each J-aggregate sample and allowed to mix. All J-aggregates dissolved in acetone over time (solutions changed colour); however, they did not seem to be affected by toluene.
This is an important result since acetone is the typical solvent use to lift-off PMMA masks in the 2-step EBL process for deterministic placement of fluorophores. Above suggests that toluene can be a suitable replacement solvent for this process.
Further experiments were performed to test this modified procedure. Four glass slides were coated with PMMA, and baked in a standard manner. These were scratched to create grooves/gaps in the PMMA mask. J-aggregate solutions of the three dyes in methanol, and S-46 in water were spun on top of the mask at low speed. Samples were immediately imaged using FLIM set-up.
From FLIM imaging, it was clear that JC-1 and PIC mostly deposit on the walls of the PMMA mask and in the "pile-up" regions. On the other hand, S-46 attached mainly to the PMMA mask when deposited from methanol. However, when deposited from aqueous mixture, its' deposition seemed to be confined to the gaps in the masks (D).
Finally, all four samples were left in toluene overnight to lift-off the PMMA mask. As expected from the initial imaging, the lift-off procedure removed all J-aggregates from samples deposited from methanol. The last sample, however, had J-aggregates remaining on the substrate (see image to the right), suggesting that this method may be practical for localised deposition of J-aggregates from polyelectrolyte solutions.

2. FLIM imaging and Cross-correlation (CC) measurements on Au rings/QDs system

FLIM and CC measurements were performed on structures consisting from a Au ring of diameter D and thickness t deposited on a quartz substrate, inside of which a ring of QDs was chemically attached to the substrate. The samples studies had Au rings of different diameters (D=350 to 450 nm) and different thicknesses (t=60 to 120 nm). QDs were either deposited in a 60 nm spot, or in a ring of increasing diameters (up to the inner diameter of the Au ring) giving a set of 5 different Au-QD separation distances for each dimension of the Au rings.
Previous observations of reduced lifetime with decreasing Au-QD separation was confirmed for Au rings of D~450 nm and t~60 nm, and was newly observed for Au rings of D~350 nm and t~80 nm. Importantly, the excitation wavelength for these measurements was different to previous measurements on these structures (488 nm instead of 405 nm). Overall, the reduction of lifetime from set 1 to set 5 (furthers to closest QDs) was less at 488 nm excitation, however, the overall lifetimes were smaller.
FLIM imaging of disks and rings of same diameters (~460 nm), with QDs deposited inside the rings/on top of disks, showed that lifetimes are significantly smaller when QDs coupled to Au rings. This suggests that observed quenching is not purely due to the presence of a metallic surface, but also due to the coupling with the plasmonic modes of the antenna. The reduction of lifetime discussed above is also evidence of this.
Finally, a set of cross-correlation measurements was performed on all of the above structures. Since all structures were permanently attached to the substrate, conventional FCS measurements were not possible. Instead, TTTR signal was recorded using 2 detectors (from 50/50 splitter), while performing an image scan of the structure. The signals from the two detectors were then cross-correlated using the SymPhoTime software (PicoQuant). The resulting CC curves deviated from the standard shape at

longer correlation times; in fact, all had an additional peak of Gaussian profile at 700-800 ms. Interestingly, the relative height of this peak to the G(0) value of the correlation curve was not constant, nor was its' width, although the latter had only minor changes. A model is currently being developed to analyse the CC data.

4) Future collaboration with host institution (if applicable)

Collaborative work on localised deposition of J-aggregates in vicinity of other structures (e.g. plasmonic nanoantennas) will be continued. Preliminary results are expected within the next two months.

Theoretical studies of the behaviour of fluorophores in vicinity of metallic nano-structrues have been discussed and planned.

5) **Projected publications / articles resulting or to result from the grant *(ESF must be acknowledged in publications resulting from the grantee's work in relation with the grant)***

Once completed, work on selective placement of J-aggregates is expected to be published in a medium/high impact journal

Results on the Au disk/QD system will be added to the manuscript being prepared for publication.

6) Other comments (if any)