

Scientific Report

PLASMON – Exchange Grant – 4067

“Investigation of plasmon enhanced supramolecular chirality of cyanine dye’s J-aggregates in direct and reverse micelles”

1. Purpose of the visit

The main aim of this visit was to further strengthen collaboration between the Nanomaterials and Spectroscopy Group at Materials Physics Centre (MPC) in San Sebastian (Spain) and Nanochemistry group at Trinity College Dublin (Ireland) leading by Prof. Y. Gunko in the area of plasmonic noble metal nanostructures and dye nano-aggregates for photonic and sensing applications.

2. Description of the work carried out during the visit

During this visit we investigated the chiroptical (absorption and circular dichroism) properties of hybrid organic/inorganic nano- and micro- structures consisting of dye molecules in J-aggregate states (arranged in direct and reverse micelles) and silver nanoparticles. The work involved: (i) the synthesis of Ag by chemical reduction of silver nitrate in water with sodium borohydride; (ii) detailed investigation of conditions of J-aggregates formation using two cyanine dyes (S8SX (FEW Chemicals) and JC-1 (Sigma-Aldrich) whose aggregation was monitored by using absorption and photoluminescence spectroscopy; (iii) improvement of the existing protocols of J-aggregate micellization which was controlled by SEM and FLIM imaging; (iv) direct investigation of chiroptical properties of hybrid nano- and micro- structures using CD and MCD spectroscopy.

3. Description of the main results obtained

The main results are observation of polyelectrolyte-induced micellization of J-aggregates, formation of reverse micelles in system of interacting J-aggregates and silver nanoparticles and strong (up to 8 times) enhancement in the optical activity of complexes of J-aggregates and silver nanoparticles as compared to CD signal from pure J-aggregates.

3.1 Experimental details

Colloidal silver nanoparticles (NPs) of 2-30 nm average size were synthesized by the conventional citrate reduction method by adding 0.8 mL of 10mM AgNO₃ to 1.4 mL of water. After adjusting the pH to 10, this solution was stirred at 0°C. Finally, 0.8 mL of 10 mM NaBH₄ was added. Doubly purified deionized water from an 18 M_Ω Millipore system was used for all dilutions.

5,5',6,6'-Tetrachloro-1,1',3,3'-tetraethyl-imidacarbocyanine iodide (JC1) carrying net positive charge and Polydiallyldimethylammonium chloride (PDDA) were purchased from Sigma-Aldrich and used without further purification.

Jasco V-630Bio and FP6600 (Jasco) were used to measure the absorption and PL spectra, respectively. CD spectra were registered using Jasco J-815 CD spectrometer.

To produce hybrid organic/inorganic nanostructures of J-aggregates/silver nanoparticles, J-aggregates (formed when cyanine dye JC1 was dissolved in water with ammonia at pH=8) were mixed with silver nanoparticles covered by polyelectrolyte PDDA in different concentration ratios. Here we use advantage of electrostatic interaction between positively charged PDDA and negative charged surface of Ag NPs. Presumably PDDA covers the whole surface of silver nanoparticle that protects the particles from aggregation and makes the colloidal solution of NPs more stable. The molecular J-aggregate of JC-1 dye interact with PDDA through anion exchange mechanism, where I⁻ anion of JC1 is exchanged for Cl⁻ of PDDA. In this case polyelectrolyte PDDA works like a linker between silver NP and J-aggregates

3.2 Optical activity of J-aggregates and silver nanoparticles separately

Figure 1 displays the absorption and CD spectra of J aggregates in a presence of PDDA (red) and without PDDA demonstrating that J-aggregates alone do not show high optical activity regardless of the presence of PDDA.

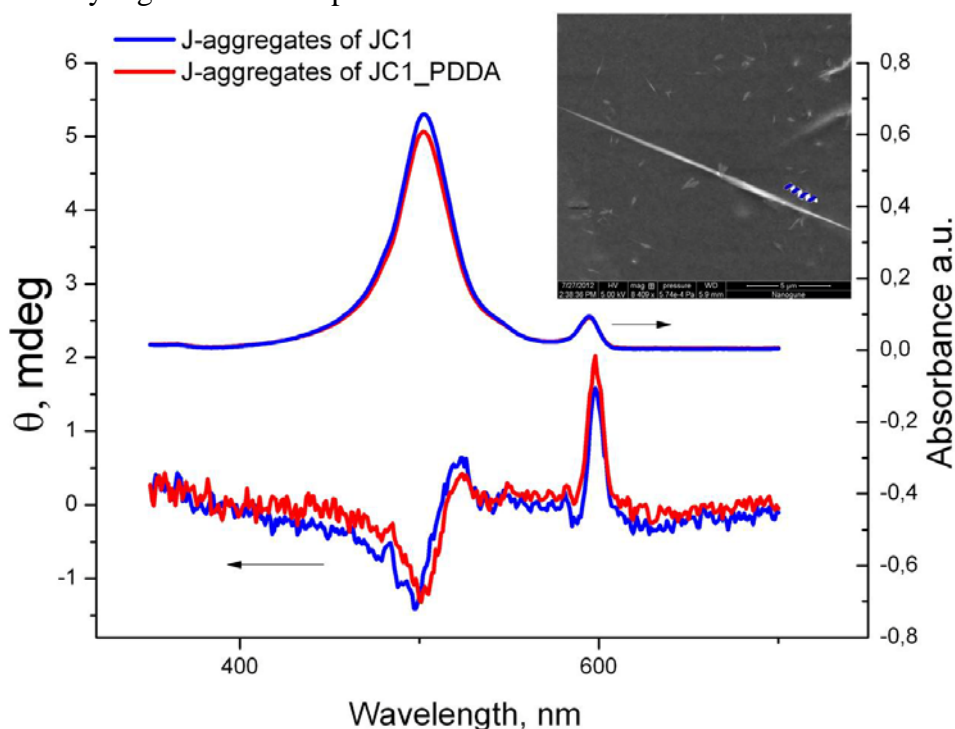


Figure 1. Absorption and CD spectra of J aggregates in a presence of PDDA (red) and without PDDA (blue curves) at pH=8 (Ammonia). Inset: Scanning electron microscope images of J-aggregates in presence of PDDA.

Generally, spontaneously formed J-aggregates of JC1 show positive Cotton effect, which is typical for left-handed helix structures (Figure 1). Indeed inset in Figure 1 presented SEM image where one can clearly see left-handed helix structure of individual rod-like J-aggregate. However, although solution contains these chiral, the CD signal from the solution is very weak.

It is noteworthy that silver nanoparticles also show very feeble, but detectable CD signal at the plasmon maximum (Figure 2). Suggested mechanisms of CD activity in plasmonic nanocrystals is the formation of chiral states on the surface of the metal nanoparticles.

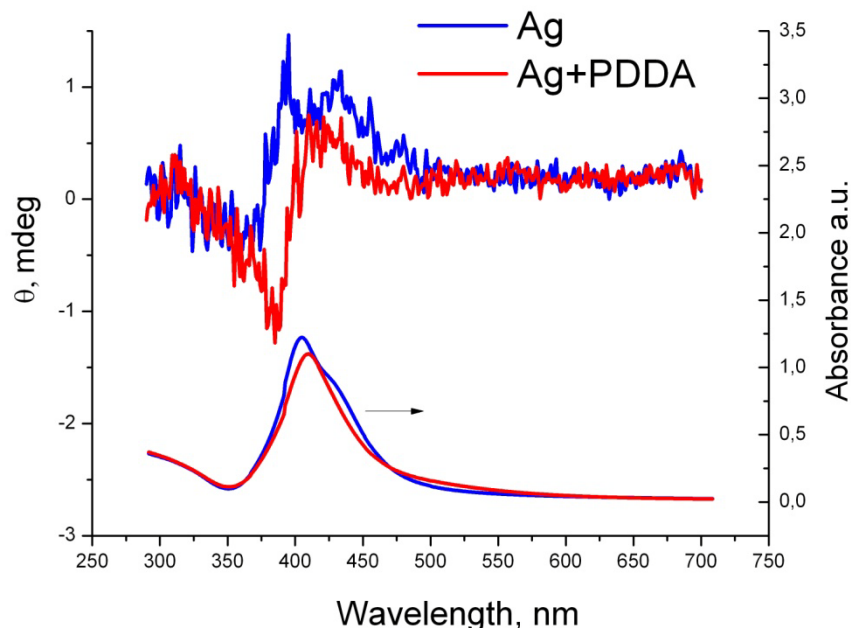


Figure 2. Absorption and CD spectra of silver nanoparticles without (blue) and with PDDA (red).

3.3 Confirmation of integration of J-aggregates and silver nanoparticles

Spectral analysis (Figure 3) and SEM imaging (Figure 4) confirmed incorporation of silver nanoparticles into the J-aggregates/Ag NP nanostructures.

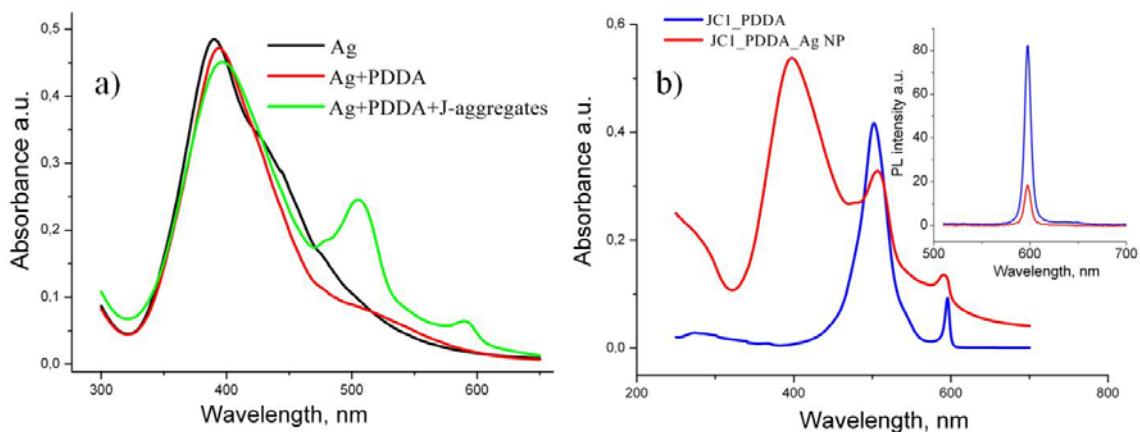


Figure 3. a) Absorption spectra of Ag NPs alone, Ag NPs with PDDA and hybrid nanostructures of J-aggregates/silver nanoparticles. b) Absorption and PL (inset) spectra of hybrid nanostructures of J-aggregates/silver nanoparticles (red curves) and J-aggregates in a presence of PDDA (blue curves).

Red shift of the plasmon peak at 400 nm proves both the interaction of Ag NPs with PDDA and with dye molecules (Figure 3a). It is well known that silver nanoparticle optical properties depend on the refractive index near the nanoparticle

surface. All bands in Ag NPs extinction spectrum shift to longer wavelengths, as the refractive index near the nanoparticle surface increases. In Figure 3 one can clearly see red shift resulting from interaction of Ag NPs with PDDA and with J-aggregates of JC1. Along with the changes in the absorption spectrum we also observed a significant quenching of the luminescence of J-aggregates in hybrid J-aggregates/silver nanoparticles complexes (Figure 3b).

Analysis of SEM images shows that interaction of J-aggregates and Ag NPs nanoparticles covered by polyelectrolyte PDDA induce the formation of spherical micelles and rod shape J-aggregates of JC1 (Figure 4a). Figure 4a clearly shows that indeed Ag NPs are integrated with micelles of J-aggregates forming the J-aggregates/Ag NP hybrid nanostructures. Ag NPs covered by PDDA stick to the surface of micelles of J-aggregates and stimulate their further aggregation, resulting in the formation of various chiral-like super structures.

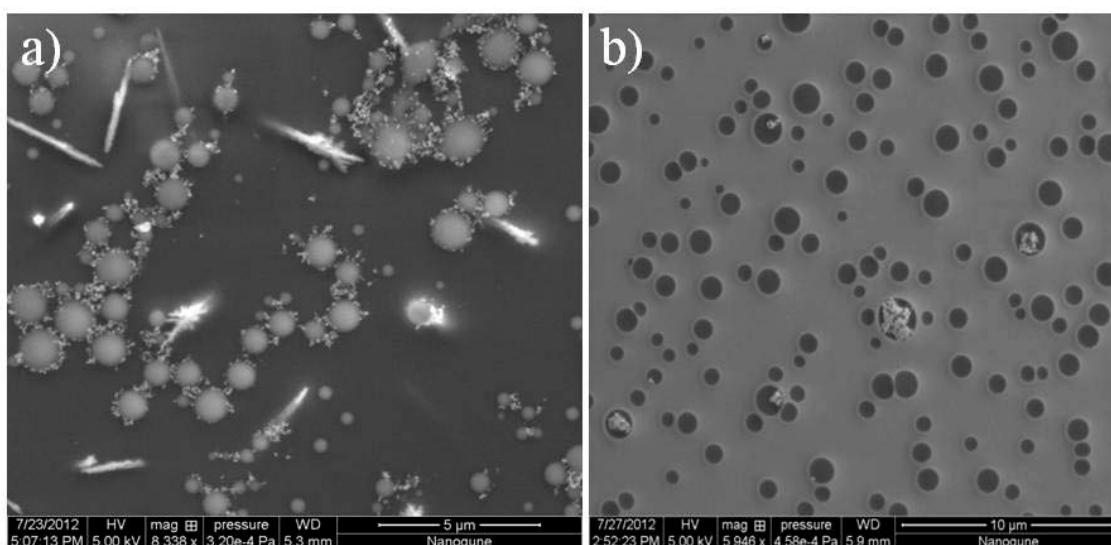


Figure 4 Scanning electron microscope images a) hybrid nanostructures of J-aggregates micelles and silver NPs covered by PDDA. b) reversed micelles of J-aggregates and silver NPs without PDDA

In contrast, while mixing J-aggregates and silver NP solution without PDDA reverse micelles of J-aggregates are formed. Figure 4b shows that Ag NPs are located inside the reversed micelles of J-aggregates and almost do not interface with dye molecules. In this case we did not detect any enhancement of optical activity of neither J-aggregates nor Ag NPs.

3.4 Enhancement of Circular Dichroism of J-aggregates by silver nanoparticles

Figure 5 demonstrate the main result of this work, namely strong (8 times) increase in optical activity of J-aggregates/Ag NPs complexes compare to CD signal of J-aggregates with PDDA and without Ag NPs. Despite the fact that Ag NPs induce the formation of spherical micelles and rod shape J-aggregates of JC1 (Figure 4), the intensity of the absorption of J-band do not changes much after injection of Ag NPs in J-aggregates solution (Figure 5).

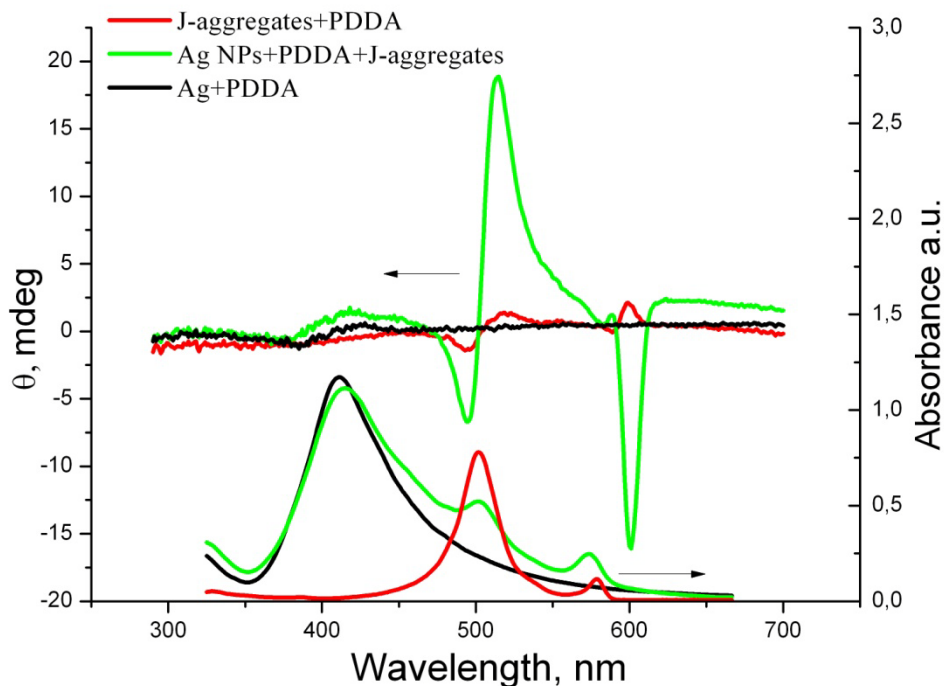


Figure 5. Absorption and CD spectra of J aggregates with PDDA (red curves), silver NPs alone covered by PDDA (black) and hybrid nanostructures of J-aggregates/silver nanoparticles (green).

However in Figure 5 one can clearly see a decrease of intensity of monomers absorption band of JC1 at 500 nm and at the same time the broadening and 5 nm blue shift of J-aggregate band originally centered at 594 nm (Figure 1), probably due to enhanced scattering of light as a result of formation of spherical micelles and rod shape J-aggregates of JC1. Also we observe equal increases in optical activity of hybrid J-aggregates/Ag NP nanostructure in spectral region of absorption J-bands and monomer of cyanine dye JC1 (Figure. 5).

Formation of hybrid organic/inorganic nanostructures of J-aggregates/Ag NP leads to the enhancement of CD activity not only J-aggregates of JC1 but also plasmonic silver nanoparticles at 400 nm (Figure 5). Optical activity of J-aggregates/Ag NP nanostructures in the region of plasmon peak is 1.5 times higher than that for Ag NPs alone or covered by polyelectrolyte PDDA (Figure 5, black curve). In figure 5 one can see enhancement of CD signal around 400 nm together with drop in intensity and red shift of plasmon absorption peak as a result of the formation of a hybrid nanostructures of J-aggregates/silver nanoparticles. These changes in absorption spectra of Ag NP together with SEM images confirm both the interaction of NP with J-aggregates and aggregation of Ag NPs.

4. Future collaboration with host institution

This feasibility study allows us to build stronger collaboration between involved research groups for further development of new advanced materials for sensing and other photonics applications. One of the next steps might be an investigation of

plasmon-exciton coupling in a hybrid system of silver nanoparticles nanostructures and J-aggregates.

5. Projected publications

We plan to report main results of this work in the paper which will soon be submitted for publication in Journal of Physical Chemistry C. EFS support will be acknowledged.