Scientific Report

PLASMON – Exchange Grant – 4698

"Study of coupling between molecular excitations in J-aggregates and surface plasmons in metal nanoparticles"

1. Purpose of the visit

The main aim of this visit was to further strengthen the 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 coupling effects in a novel type of hybrid structures that combine plasmonic nanoparticles with organic dye molecules in J-aggregate state. SEM imaging and absorption spectroscopy were used in this work. Main goal was to investigate how coupling strength depends on detuning of plasmonic absorption bands from the excitonic resonance of J-aggregates.

3. Description of the main results obtained

Three plasmonic nanoparticle systems made of Au, Ag and alloyed Ag/Au were investigated in this project. The best results among these have been obtained for Au nanostars with different lengths of spikes. The main results are the observation of strong exciton/plasmon coupling observed in absorption spectra of gold nanostars covered by the shell of J-aggregates which manifested itself in the splitting of absorption bands and the development of an approach for the correct estimation of the value of the energy of Rabi splitting.

3.1 Experimental details

Gold nanostars with different length of spikes (therefore with different positions of the associated absorption bands) were synthesized in an aqueous solution using cetyltrimethylammonium bromide (CTAB) as the capping and growth-regulating agent.
Transmission electron microscopy (TEM) image of nanostars and absorption spectra of nanostars with different lengths of spikes are shown in Figure 1.
J-aggregates were formed from the following two dyes: JC1 (5,5',6,6'-tetrachloro-1,1',3,3'-tetraethyl-imidacarbocyanine iodide) and THIATS ((3,3′-bis-(3-sulfopropyl)-5,5′-dichloro-9-ethylthiacarbocyanine): for chemical structures, see Figure 2a,b. J-aggregates of both dyes form spontaneously upon dissolution of the dye in the deionized water at pH7.

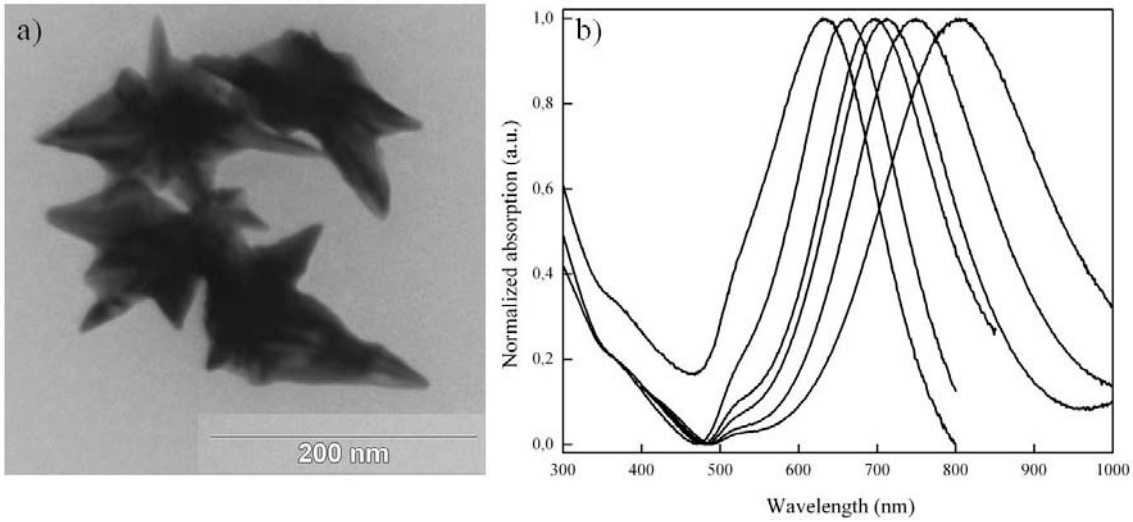

Figure 1. TEM image of star-shaped gold nanoparticles (a) and absorption spectra of nanostars with different lengths of spikes.

The reason why these particular dyes were chosen was that upon the aggregation they develop very narrow absorption bands (J-bands) both located very close to the maximum of nanostar absorption (Figure 1b and 2c) which favors the regime of strong plasmon-exciton coupling in the hybrid systems.

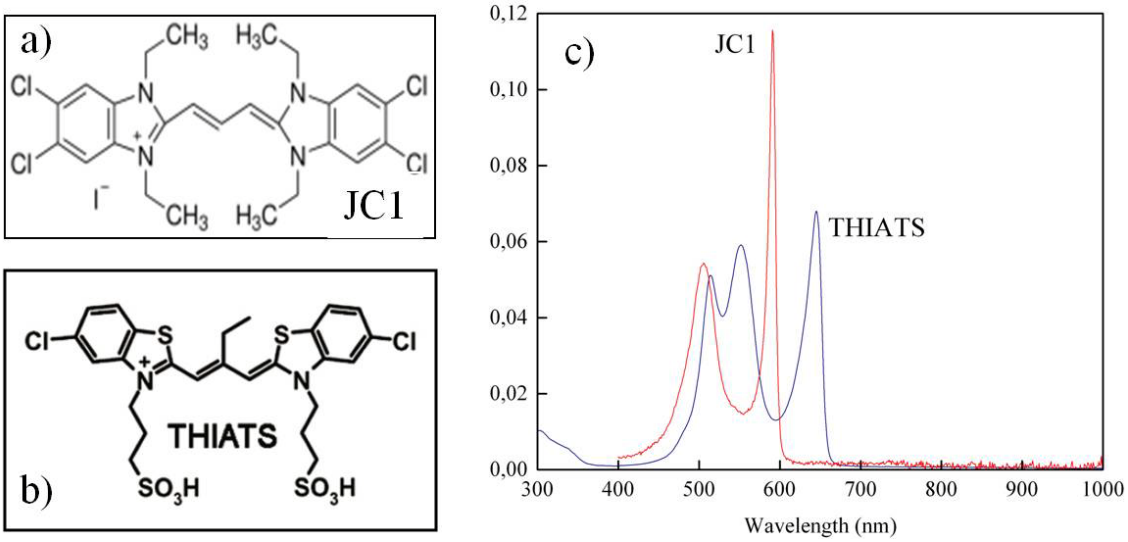

Figure 2. Chemical structures (a,b) and absorption spectra of J-aggregates of JC1 and THIATS dyes.

The J-aggregates of JC1 and THIAS exhibit a narrow absorption J-bands centered at 591 nm and 645 nm, respectively. Because the shapes of absorption and fluorescence bands were not symmetrical and sometimes affected by instrumental artifacts, we postulate that full width at half maximum (fwhm) = 2 × hwhm, where hwhm (half width at half maximum) was measured for the “red” side of the absorption band. Using this approach, values of fwhm were estimated to be 8.4nm and 14.8 nm for JC1 and THIAS, respectively, which are much smaller than the linewidth of the nanostars. Thus, one of the requirements for strong coupling is satisfied.

Hybrid structures of gold nanostars and the J-aggregates of the dyes were produced by the addition of the concentrated ethanol solution of the dye to an aqueous solution of

gold nanostars in the presence of ammonia at pH8. Interactions between nanostars and molecules of J-aggregates resulted in the formation of chainlike tightly bound agglomerates of gold nanostars interconnected by an organic matter. These agglomerates were separated from the excess of dye molecules or J-aggregates not bound to gold nanostars by centrifugation at 3,800 rpm for 2 min and then redispersed in aqueous solution.

3.2 Plasmon-exciton coupling in a hybrid system of gold nanostars and J-aggregates

Main results of our study are presented in Figure 3 and Figure 4. In the hybrid structure of both nanostars and J-aggregates, the pronounced dip at 590 nm (Figure 2) and 645 nm (Figure 3) (which corresponds to the absorption wavelength of the J-aggregates of JC1 and THIATS dyes, respectively) appears as a result of strong coupling of the excited states of J-aggregates and plasmon modes of the nanostars. Also it can be seen that the separation between short-wavelength and long-wavelength peaks grows with detuning of absorption peaks of gold nanostars with different lengths of spikes from excitonic resonance of J-aggregates (Figures 5a and 6a). This separation reaches 614 (Figure 5,b) and 406 meV (Figure 6b) for biggest detunings observed in this work for J-aggregates of JC1 and THIATS dyes, respectively. However, because the coupling between plasmonic and excitonic systems requires resonant condition (i.e. matching of plasmonic and excitonic resonances), one can hardly assume that these values reflect the correct values of the energy of Rabi splitting.

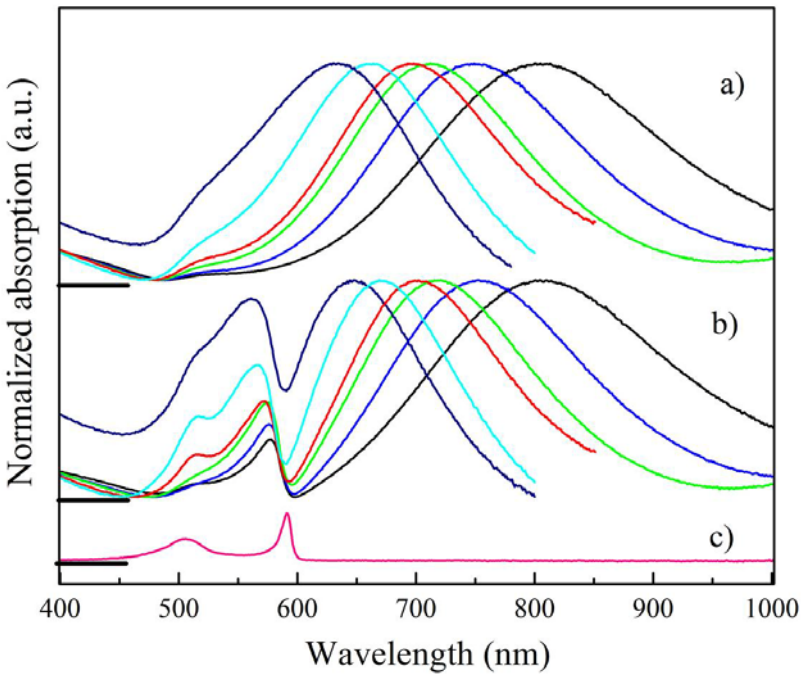

Figure 3. Absorption spectra: of star-shaped gold nanoparticles with different lengths of spikes (a), J-aggregates of JC1 dye (c) and hybrid system of nanostars with different lengths of spikes and J-aggregates.

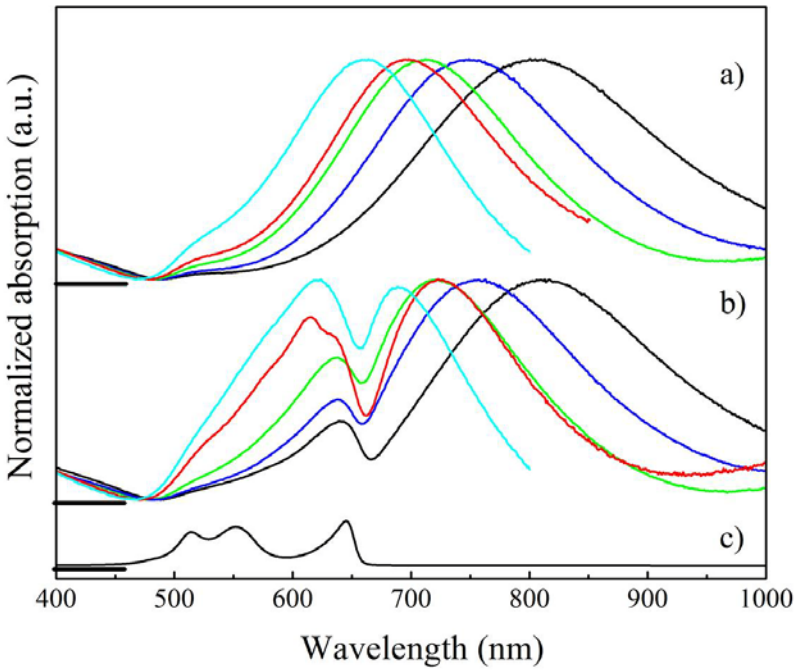

Figure 4. Absorption spectra: of star-shaped gold nanoparticles with different lengths of spikes (a), J-aggregates of THIATS dye (c) and hybrid system of nanostars with different lengths of spikes and J-aggregates.

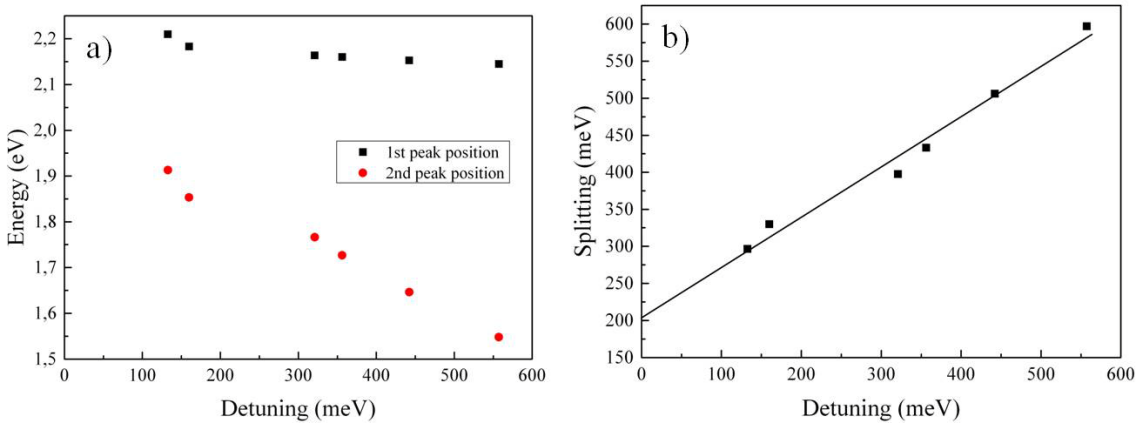

Figure 5. Spectral positions of high energy (short wavelength) and low energy (long wavelength) peaks in absorption spectra of hybrid system of nanostars with different lengths of spikes and J-aggregates of **JC1** dye versus detuning of these peaks from the excitonic resonance (a). Panel (b) shows estimated values of the splitting versus detuning. Solid line is a result of linear fitting.

Unfortunately, experimentally it is difficult to provide exact matching of abovementioned resonances. For example, the minimum detuning detected in our experiments with JC1 J-aggregates and Au nanostars is 133 meV (Figure 6a) whereas for THIATS dye this value was estimated to be 52 meV.

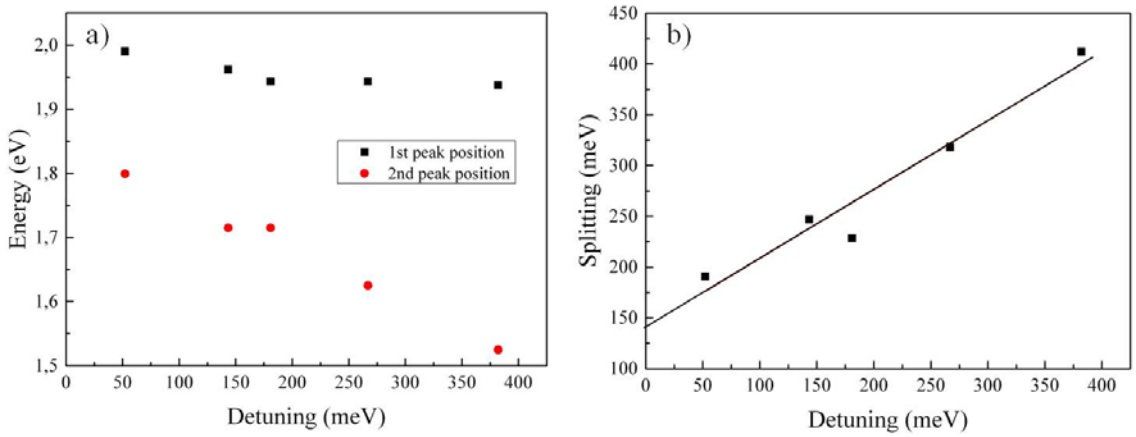

Figure 6. Spectral positions of high energy (short wavelength) and low energy (long wavelength) peaks in absorption spectra of hybrid system of nanostars with different lengths of spikes and J-aggregates of **THIAS** dye versus detuning of these peaks from the excitonic resonance (a). Panel (b) shows estimated values of the splitting versus detuning. Solid line is a result of linear fitting.

In order to obtain the correct values of the energy of Rabi splitting, which correspond to the resonant conditions, using data presented in Figures 3 and 4, we extracted the plasmon and molecular resonance positions, as well as positions of low-energy and high-energy peaks in the spectra of hybrid systems (denoted as 1st and 2nd peaks, respectively) and plot them as a function of detuning (Figure 5b and 6b). In both cases the dependence of spectral splitting on the detuning can be well approximated by linear function, which allowed us to estimate values of the splitting for resonant conditions (i.e. zero detuning). By this way values of the energy of Rabi splitting were estimated to be 202 meV and 141 meV for hybrid systems based on J-aggregates of JC1 and THIATS dyes, respectively.

4. Future collaboration with host institution

This study allows us to build stronger collaboration between involved research groups for further development of new advanced materials for sensing and other photonics applications.

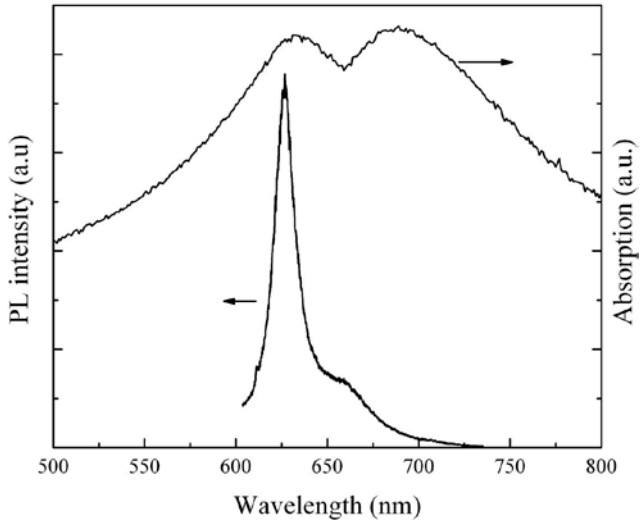

Figure 7. Photoluminescence and absorption spectra of hybrid system of gold nanostars and J-aggregates of THIAS dye.

One of the next steps might be the investigation of plasmon-exciton coupling effects in photoluminescence spectra of the hybrid systems, the field which is remains largely unexplored. Our initial results, one of which is presented in Figure 7, clearly demonstrate feasibility of this study. From the other hand, based on our preliminary results, this research can be considered as strongly challenging mostly due to the interplay between the coupling effects and photoluminescence quenching by metal nanoparticles.

5. Projected publications

We plan to report main results of this work in paper which will soon be submitted for publication in ACS Nano. EFS support will be acknowledged.