Scientific Report

PLASMON - Short Visit Grant – 4437

"Development of hybrid system of plasmonic nanoparticles and J-aggregates with chiral properties"

1. **Purpose of the visit**

The aim of this visit was to establish research collaboration between Nanophotonics Group at Materials Physics Center (Donostia-San Sebastian, Spain) and Group of Professor Yurii Gun´ko (School of Chemistry, Trinity College Dublin).

2. **Description of the work carried out during the visit**

During this visit we investigated chiral properties of J-aggregates and developed an approach to form chiral composites using assembly of metal nanoparticles (both Au and Ag) and J-aggregates of cyanine dyes. The hybrid samples of various com were also studied by z-scan technique during the visit of Professor Yury Rakovich (Short Visit Grant No. 4436).

3. **Description of the main results obtained**

The main results are development of new hybrid system consisting of Ag nanoparticles and nano-aggregates of cyanine dye and observation of strong enhancement of chirality in this hybrid system.

First, we have studied the optical properties of a water soluble cyanine dye S 2165 (FEW Cemicals): 2-[3-[1,1-Dimethyl-3-(4-sulfobutyl)-1,3-dihydro-benzo[e]indol-2-ylidene]-propenyl]-1,1-dimethyl-3-(4-sulfobutyl)-1H-benzo[e]indolium hydroxide.

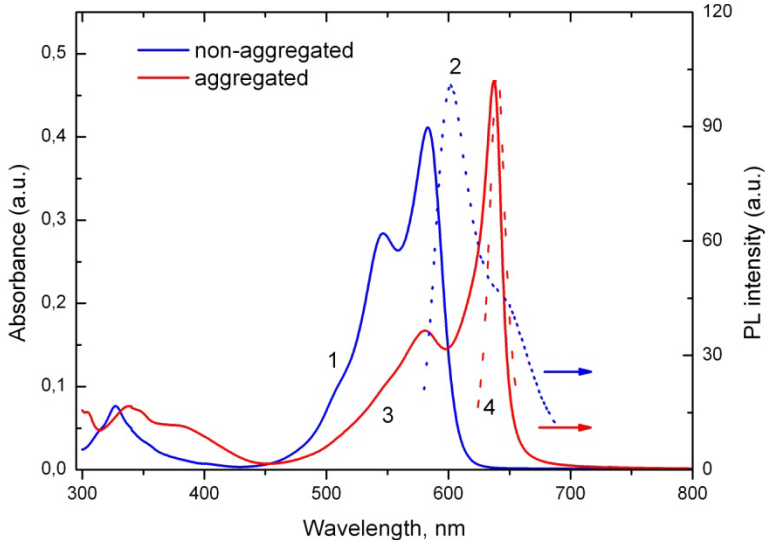

Fig. 1. Absorption (1,3) and PL (2,4) spectra of non-aggregated and aggregated dye

The absorption spectrum of non-aggregated dye in aqueous solution contains the dimer and monomer bands centered around 545 nm and 538 nm, respectively. A new band at λ = 639 nm (J-band) appears upon aggregation stimulated by addition of polyelectrolyte

Poly(ethyleneimine) (PEI) PEI (Figure 1) or NaCl. Formation of J-band is caused by Coulomb coupling of the transition dipoles and delocalized nature of the electronic excitations in aggregates.

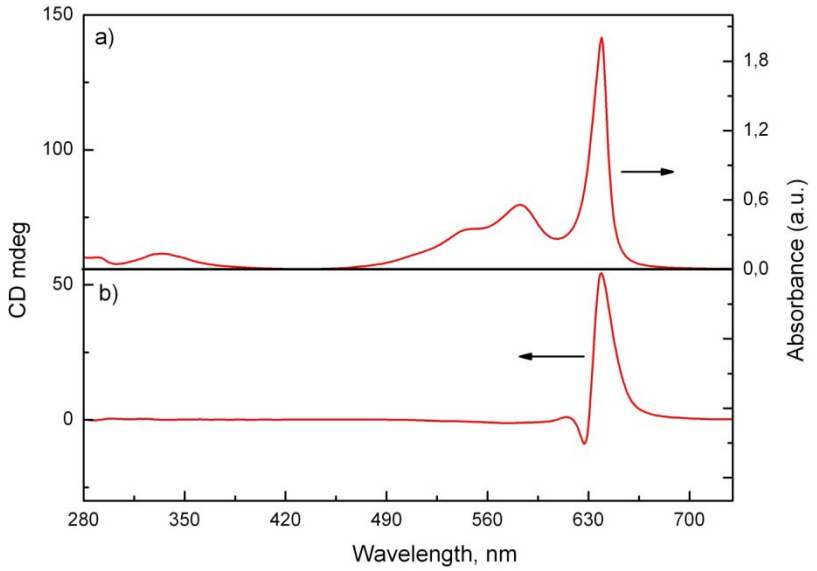

Figure 2. Absorbance (a) and CD (b) spectra of S2165 aggregated by addition of NaCl.

Together with absorption spectroscopy, circular dichroism (CD) measurements were carried out. As can be seen from Figure 2, the introduction of 0.2M NaCl in 10^4M aqueous solution of S2165 results in formation of J-band (Fig. 1,a) and a bisignate CD signal (Fig. 1,b): a positive band, which maximum coincides with absorption maximum of J-band and a negative band with dip centered around 626 nm, corresponding to positive chirality. No CD signal originating from monomer was found. No change in lineshape was detected upon increasing or decreasing the concentration of aggregated dye in this sample.

Quite different behavior was observed when dye was aggregated by trace amount of PEI.

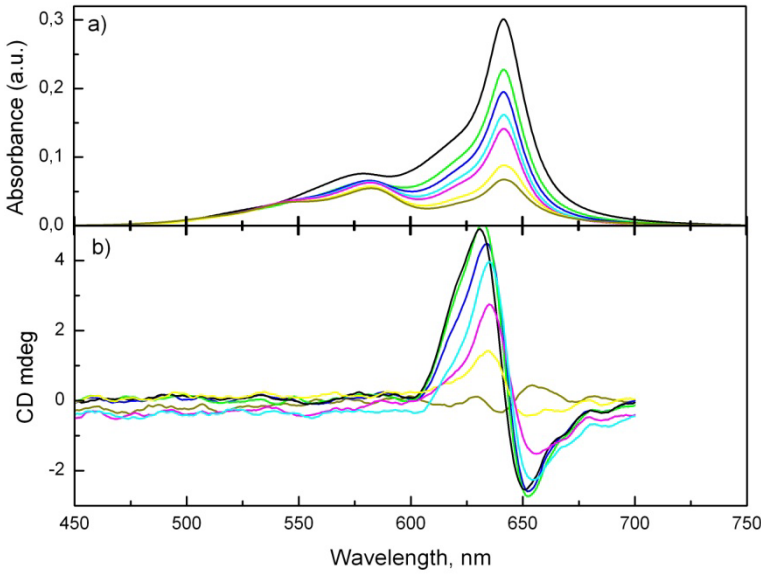

Figure 3. Absorbance (a) and CD (b) spectra of S2165 aggregated by PIE.

In present of small amount of PIE we can see positive bisignate CD signal, but increase in concentration of polyelectrolyte results in reversion of chirality of nano-aggregates: the positive bisignate CD signal reverses to a negative one. This result is not only significantly different from the case of NaCl induced nanoaggregates, but also from previous report where template J-aggregates, exhibit either positive or negative chirality.[1, 2] There are however some other differences in lineshapes of absorption and CD spectra of NaCl- and PIE- induced nanoaggregates. First, absorption linewiths of these two samples differ by 10 nm. Moreover, small shoulder around 620 nm can be seen in CD spectra of PIE-aggregated dye. Another difference is the fact that not CD dip, nor CD maximum in spectra of this sample do not coincide with maximum of absorption band (Fig. 2a,b). The origin of these effects is not well understood yet and has to be further investigated.

We also investigated the properties of hybrid system consisting of J-aggregates and colloidal silver nanoparticles (NPs). Ag NPs of ~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 $NaBH_4$ was added. It turned out that strength of CD signal from J-aggregates can be can be further enhanced by combining them with these nanoparticles. This can be seen in Figure 3.

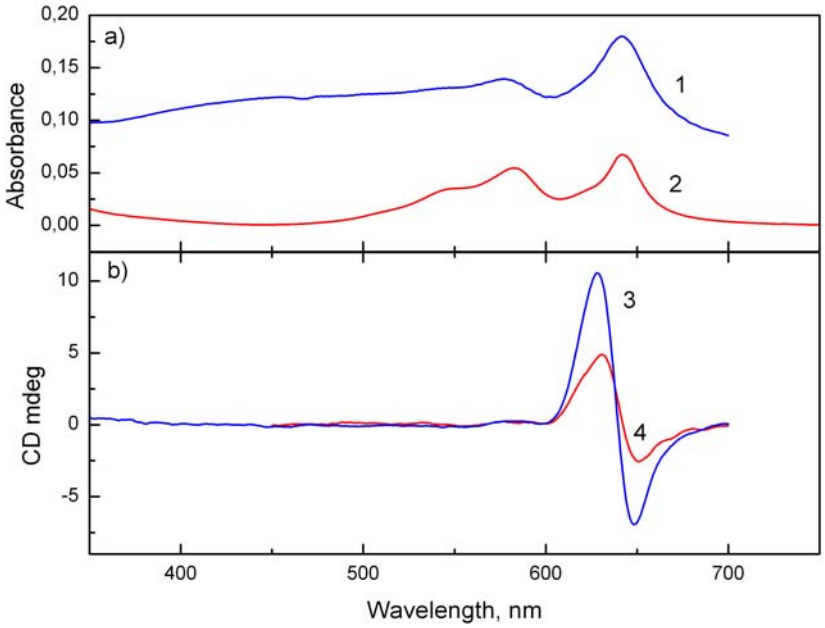

Figure 3. Absorbance (a) and CD (b) spectra of S2165 aggregated by PIE without (curves 2 and 4) and with Ag NPs (curves 1 and 3).

The origin of this effect is not understood yet and has to be further investigated.

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. As the next step extra research work is required to explain transition from positive to negative chirality of J-aggregates and strong enhancement of chirality by Ag nanoparticles.

5. Projected publications

After clarifying the origin of observed effect we plan to report main results of this work in one of high impact factor journals, tentatively in Angewandte Chemie. EFS support will be acknowledged.

References

1. Kim, O.-K., et al., *Super-Helix Formation Induced by Cyanine J-Aggregates onto Random-Coil Carboxymethyl Amylose as Template.* Journal of the American Chemical Society, 2005. **128**(2): p. 510-516.
2. Wang, M., G.L. Silva, and B.A. Armitage, *DNA-Templated Formation of a Helical Cyanine Dye J-Aggregate.* Journal of the American Chemical Society, 2000. **122**(41): p. 9977-9986.