Title	Design, preparation and advanced spectroscopic characterization of chiral colloidal plexcitonic nano hybrids for quantum nano photonic applications

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# months (min.3)	3

Project description (2 page max):

This project focuses on the design and preparation of colloidal supramolecular systems characterized by strong coupling among the different interacting components, and on the investigation of coherent and incoherent ultrafast dynamics.

The strong coupling regime is a unique interaction regime that promises to play a crucial role in quantum optical research. When a strong coupling is established between two systems A and B, new hybrid eigenstates are expected to arise. This new strongly coupled A-B system will generally have different electronic and optical properties than the two non-interacting individual systems A and B.

A first typical example of strong coupling regime is the formation of molecular exciton states. When different molecules strongly interact through their dipole moments, new eigenstates are formed, called excitons, described as 'collective', delocalized electronic excited states arising from coherent superpositions of excitations of molecules in the assembly. Examples are molecular crystals, nanoscale self-assembled structures like H or J aggregates, and light-harvesting systems in photosynthesis. [*Nature Mater* **2006**, 5, 683] It has been recognized that excitons play a fundamental role in the mechanism of electronic energy transfer, which can notably include quantum coherent dynamics, in various synthetic nanoscale and biological systems [*Chem Soc Rev* **2013**, *42*, 4932]. A second example of increasing complexity is the strong coupling between molecular excitons and confined light fields, for example, those associated with a plasmonic nanomaterial [*Langmuir* **2023**, 39, 36, 12793]. This coupling leads to the formation of new hybrid states called plexcitons (plasmon+exciton), states that inherit both molecular and plasmonic properties. For example, we optimized the preparation conditions and studied the photophysical properties of plexciton systems built by coupling porphyrins J-aggregates with gold nanospheres [*Nanoscale* **2021**, *13*, 6005] and cyanine J-aggregates with gold nanourchins [*JPCC* **2021**, *125*, 19897]. What is still largely underexplored is the dynamic properties of these hybrid states. Only a handful of dynamics measurements have been proposed so far [*JPCLett* **2022**, 13, 6412; *Adv Opt Mater* **2023**, 2203010], and at present, it is not clear how the lifetimes of the coupled states are related to the initial plasmon-exciton states, nor the coherent properties of these states have been characterized. To fill this gap, the project will employ state-of-the-art time-resolved techniques including multidimensional coherent spectroscopies [*JPCC* **2021**, 125 (2021)1 3096; *NaturePrimer* **2023**, 3, 84].

The emergence of different coupling behaviors can be governed by various combinations of the coupled units, as well as the spatial arrangement and relative orientation of the individual components. Working with

colloidal materials, this can be achieved by tuning the experimental conditions used for the sample preparation. The possibility of sculpting the energy spectra and the optical properties of these strongly coupled materials in a relatively easy chemical way, tuning the supramolecular conditions used for their preparation, are surely highly promising for a variety of applications, including room-temperature quantum optics, biosensors, nanoscale light sources, and nanoscale energy transport.

One of the most recent approaches proposed in this context is exploiting chiral coupling as a new dimension to control interactions. Understanding the chiroptical characteristics of chiral excitonic and plexcitonic systems enriches the general principle of strong coupling and provides direct guidelines for the design of numerous chiroptical devices. Furthermore, chiral plexcitonic nanostructures move the manipulation of chiral electromagnetic fields to the nanoscale, which provides an additional degree of freedom in terms of adjusting the coupling between the different units. Only a handful of papers are currently available on this topic and still a lot of work must be done.[*ACS Nano* **2021**, *15*, 2292]

The realization that the chemical properties of molecules can be changed in a reversible manner by strong coupling to light through the establishment of strong -possibly chiral- interactions with a plasmonic nanoparticle is therefore a relatively new approach. The technological applications of this research field are still in their infancy; therefore, it is expected that the main outcomes of this project will mainly provide fundamental advancements in the current knowledge of the photophysical and ultrafast dynamic properties of complex multichromophoric hybrid chiral nanomaterials.

Overall, the ability to control the light-matter interaction at the nanometer scale is one of the major tasks in all nanophotonics applications. Besides their importance for fundamental studies of light-matter and many-body interactions at the nanoscale, excitons and hybrid molecular-plasmon states promise to unlock an unprecedented capability of directing the migration of excitation energy at the nanoscale, offering exciting prospects in light-harvesting and all-optical circuit architectures and in general for all those photonic applications that require strict control over the flow of energy in time and space.[*Nanoscale* **2021**,*13*, 6005]

The main general objective of this project is to exploit the strong coupling regime in excitonic and plexcitonic systems to prepare nanomaterials with tailored optical properties. In particular, we want to use chirality as a new knob to tune and control the interactions between molecules in molecular aggregates or between molecules and plasmonic nanoparticles in plexcitonic materials. Our first objective will thus be to prepare a library of strongly coupled (excitonic (obj 1) and plexcitonic (obj .2)) systems. Particular attention will be paid to investigating the ultrafast coherent dynamics of different nanoassemblies characterized by different opto-chiral properties and identifying possible structure-to-properties relationships towards potential applications of these materials in real nano-optic devices (obj 3, task 3.1). To this aim, novel spectroscopy techniques sensitive to the ultrafast dynamics of chiroptical samples will also be developed (obj 3, task 3.2).

	Objective	***Associated Tasks***
1	Chiral excitonic systems	1.1 Design and preparation of chiral (and achiral) molecular aggregates 1.2 Preliminary basic characterization
2	Chiral plexcitonic systems	2.1 Design and preparation of chiral (and achiral) plexcitonic nanohybrids using different nanoparticles and molecular moieties. 2.2 Preliminary basic characterization
3	Nonlinear ultrafast optical proprieties (coherent and incoherent dynamics)	3.1 Study of the optical properties of the most promising nanohybrids with time-resolved techniques (pump-probe, multidimensional electronic spectroscopy) 3.2 Realization of an optical setup for chiral sensitive time-resolved technique