STATE-OF-THE-ART

Realization and adoption of efficient quantum computing principles would revolutionize many aspects of everyday life by vast acceleration of computation and by bringing the possibility to solve problems that are not addressable by conventional resources. The core functionality of any quantum computer is built upon a two-state element - *a qubit* - which in contrast to classical bits can not only be in the '0' and '1' states but also in their *coherent superposition.* That requires physical systems in which the phenomenon of quantum entanglement occurs and dominates with sufficient spatial and temporal coherence. Among the potential objects of interest are optical cavities,[1,2] trapped ions,[3-5] molecular spins,[6,7] Josephson junctions,[8,9] quantum dots[10] and solid state color centers,[11,12] which all have their unique advantages but also practical limitations. One of the great opportunities in quantum computing are molecular arrays, since they could be harnessed into functional blocks through chemical tuning and self-assembly, thus allowing them to be *programmable and scalable*.

Although the electron spin has been in the focus of research on molecular qubits, perhaps the first example of **quantum entanglement in physics has been demonstrated in molecular aggregates** of organic chromophores sharing delocalized electronic excitations[13] - *excitons*. Theoretically it has been suggested that building quantum bits and quantum-logic gates from dyes is possible by tailoring the chromophore geometries and couplings in an aggregate (scheme in Fig.1) in order to encode specific quantum transformations[14,15] that realize the elementary quantum computing operations,[16] robust against environmentally-induced decoherence. Techniques that have ultra-high spatial selectivity will be naturally paramount to any efforts in this direction. There are two major challenges to this approach: first how to exactly control the molecular units arrangement within an aggregate and second, how to promote a system into a particular entangled excitonic state and follow the evolution of the state. Therefore new concepts and methodological approaches are urgently needed.
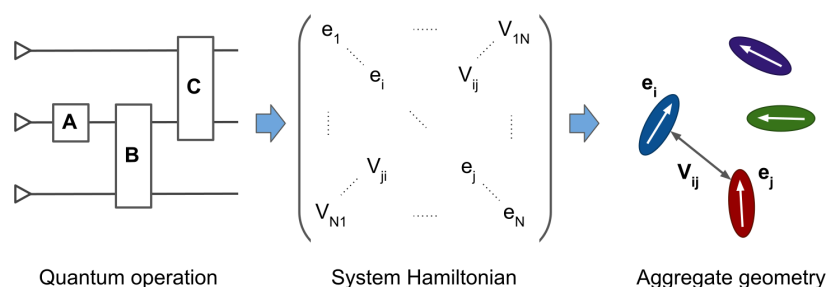

Fig.1: Encoding a quantum operation, via translation to a Hamiltonian
and realized by specific geometry of an excitonic aggregate made of
molecular dyes with on-site energies e_i and interactions V_{ij}.[14]

Strategies as supramolecular support structures[17,18] (e.g. proteins), metal-organic scaffolds[19] or DNA-templating[20] have been trialed in order to attain control over the mutual orientation and distances of the molecules. New appealing alternatives for achieving **a precise control over the aggregate geometry** emerge from research of **2D self-assembly**.[21,22] There is a wealth of experience in the surface-science community with preparation of clean crystal surfaces and growth of well-defined ultrathin inorganic and organic layers, by applying chemistry and physics approaches. Moreover, we are witnessing an increasing number of experiments where clusters are formed from suitable precursors on dielectrics,[23-26] in order to effectively decouple them from the metallic substrates leading to a general enhancement of the excited state lifetimes. The potential in this area grows rapidly as new routes to aggregate formation and new promising dielectric substrates are being explored and adopted.

Optical *far-field* spectroscopy has been proposed for **inducing and probing the states of the excitonic circuits**, i.e. using polarized light to distinguish between the inputs and outputs.[14] However, this approach is fundamentally limited to a spatial resolution of a few hundred nanometers which precludes any deep understanding of the model systems, because with a spatially uniform electric field over the aggregate, for many relevant cases, most of the excited states are inaccessible to the far-field spectroscopies and thus referred to as *dark*. This problem

has a solution: in **the application of nano-optics and *tip-enhanced microspectrocopies.*** This permits to concentrate optical fields at the single molecule-scale and allows addressing photophysics of individual absorbers/emitters in excitonic circuits, including their dark states.[27] A methodology based on these principles could gain advanced control and access to the excitonic evolution. This is a unique opportunity to tackle the dynamics of individual excitons, and its dependence on the geometry of self-assembled structures, with submolecular resolution. Ultimately such mechanistic understanding can lead even to the development of paradigm photonic circuits and quantum computers.

A platform perfectly suited for creation and analysis of individual molecular aggregates is the **cryogenic scanning probe microscopy (SPM)**, working in ultra-high vacuum (UHV) environment. Single-crystal metallic samples, ultrastable molecular adsorbates and well-defined atomically-sharp metal tips controlled with picometer precision are the native setup for the vast majority of the experiments performed in the UHV SPM instruments, which makes them ideal for ensuring highly-controlled parameters of the model excitonic circuits. The typical SPM setups are highly versatile and rich in the selection of the analytical tools they offer: a variety of electron and force spectroscopies; external electric, magnetic or force fields can be also applied and electron spins can be probed. Recently, **optical spectroscopy that uses the scanning tip as the nanoplasmonic antenna** has become a part of the UHV SPM toolbox.[28-30]

The past decade has seen a vigorous progress in SPM techniques, stemming from integration of independently evolving methods into a single instrument. The most remarkable with a promising future and a number of successful applications is the **combination of atomic force microscopy (AFM) and scanning tunneling microscopy (STM)** within one sensor,[31] which permit simultaneous access to the electronic properties and atomic forces on single molecules. The power of the individual techniques has been repeatedly demonstrated by spectacular images of diverse molecular backbones,[32-38] taken with an unprecedented spatial resolution. I have actively contributed to the advances in the AFM/STM, developing new methodologies of mapping the electrostatic charge on molecules,[39] demonstrating and explaining imaging by inelastic electrons[32,39] and probing new tip functionalizations and sharpening methods.[32,39-41] With my colleagues, we applied the AFM/STM technique to discover new phenomena, e.g. chirality transfer in surface chemistry,[42] spin-crossover of non-covalently doped molecules,[38] quantum interference of dopants in graphene,[43,44] diversity of azide transformations on metal surface,[45] Kondo physics on a single molecule,[46] and to elucidate structures of new materials.[47,48]

The rapid **development of optical STM techniques** unlocked a completely new level of future research of photophysics in condensed matter, with particular interest in organic molecules. The new approach - the scanning tunneling microscopy-induced luminescence (STML) has been successfully applied to detect emission of individual molecules and ignited an interest in the technique.[28,49-54] Here, contrary to the conventional *far-field* spectroscopic methods, the excited states can be induced *locally* by either injecting electrons or channeling external photons into the junction via the tip-sample nanocavity, allowing collecting *photon maps*. The spatial resolution of the photon collection is extremely high, because the quantity of detected photons is augmented by optical modes in the tip-induced plasmon gap, which promotes radiative decay of molecular excitations due to the Purcell effect. The STML represents a very significant advance in the methodology, because it adds access to the energetics of the excited states, and allows picosecond time-resolution measurements that open the door to detect transient ultrafast phenomena within single molecules. **Our team has contributed to the advances in this field**, e.g. by demonstrating STML was possible with the identical tips as the STM/AFM[55] and addressing the role of the tip functionalization in the photon mapping. Recently we have showcased the influence of the external fields on single-molecule emission[56] and measured excitonic lifetime on picosecond timescale with a newly developed application of phase fluorometry.[57]

From a theoretical point of view, it is known that the delocalized excitonic states arising upon aggregation critically depend on the property of the chosen elementary molecular units and on the aggregation morphology.[58] Therefore, much effort from the theoretical perspective is devoted to shed light on the structure-property relation in aggregate systems, trying to rationalize how the interchromophoric arrangement influences the optical properties of the aggregates,[59-61] and

aspiring to design them with custom functionality in mind.[62,63] **Quantum-chemical (QC) ab-initio computational methods can provide an accurate description of the many-body photophysical properties of isolated molecules and their aggregates**, allowing to reliably access information on the energy and the optical response of the excitonic states. The application of dedicated analysis approaches allows obtaining deeper information on the nature of the excited state *(locally excited or charge transfer)* and on the underlying interactions (*couplings*) governing the photophysics.[64-67].

However, there are limitations to the theoretical description that need to be overcome. For larger arrays of molecules, where excitons can be delocalized over several molecules, the applicability of full QC protocols could be severely limited by the system dimensions. For such cases, simpler **parametrized exciton models** allow to capture the essence of the problem at an affordable computational cost.[64,68-70] Furthermore, in the STML experimental measurements, the excitonic emission is strongly modulated by the structure of the optical field in nanocavity created by the tip. Conveniently placed nanocavities can in principle access such aggregate states, which are otherwise dark in the conventional far-field spectroscopy.[27] Taking into account the effect of the near-field light-matter interaction with the emitting aggregate will be instrumental in correctly relating the QC theoretical predictions of aggregate emission with the experimental spatially-resolved hyperspectral data (photon maps). This is possible to achieve via specialized **photon map simulation tools**.[71,72] As yet, such general photon map simulation programs are not available and their development is highly desirable for the future general development of the STML field.

With the powerful synergy of techniques offered by the cryogenic UHV SPM with optical access, we can routinely perform very complex tasks on individual molecules and molecular assemblies. It is possible to precisely identify the adsorption geometry of molecules, measure electrostatic charge,[39,73-75] break/create chemical bonds on their periphery,[76,77] manipulate them to obtain defined artificial structures[78] and analyze with all the methods mentioned above. Here, the application of the STML together with the addition of a suitable theoretical description and photon map simulation tools are timely and highly relevant in the investigation of various types of aggregates with entangled excitonic states that can be promising candidates for optical quantum gates.

BEYOND THE STATE-OF-THE-ART

To tackle the problem of tailoring and addressing well-defined molecular aggregates with entangled excitonic states using the cryogenic UHV SPM, a multilateral approach is needed that would rely on: i) the choice of the experimental aggregate system and its successful realization, ii) an appropriate interpretive theoretical framework, with a proxy computational tool mediating the comparison of the raw experimental data with first-principles theoretical calculations. Each of the points requires developing **new strategies, specific to 2D molecular aggregates adsorbed on insulating crystalline substrates, and their detailed analysis in a nanocavity.** To this end, we will exploit the available expertise in the field, our best knowledge and experience to go beyond the state-of-the-art.

One particular **challenge is creating small excitonic clusters,** consisting of a few molecular units in specific geometries. The clusters have to be sufficiently decoupled from the base metal electrode in order to avoid exciton quenching, which can be achieved by inserting a thin film of a wide-bandgap material between the metal substrate and the cluster. The most common examples of this approach are based on growing thin films of NaCl or KCl on atomically clean low-index surfaces of metal crystals.[79] These salts exhibit a carpet-like growth typically with the 001 surface termination.[80] We will deposit molecular emitter precursors by thermal deposition on such substrates keeping them at temperatures below 10K to avoid diffusion. Subsequent formation of clusters can be achieved **by manipulating the molecules** with the SPM tip to desired locations **or thermally by low-temperature annealing** (50-150K),[23-26] promoting a moderate diffusion on the salt surface.[51,81-83] With the manual approach, various artificial cluster shapes can be formed. However, not all molecules can be manipulated easily to achieve the desired placement and orientation, and the structures crafted by manipulations generally are not stable beyond the

temperatures of their creation, not to mention the time demands for such undertaking. That is the advantage of adopting the latter approach, in which the clusters naturally form by diffusing on top of the insulator islands, without spilling over to the bare metal.

Because of a very limited choice of suitable examples of aggregate thermal formation on salts in the literature,[23-26] **we successfully tested this novel concept** ourselves on a well-known dye precursor, perylene-tetracarboxylic dianhydride (PTCDA) flat-adsorbed on NaCl on Ag(111), annealed to 80-120K. After inspection with the SPM back at the base temperature below 10K, we found an abundance of 2D aggregates (see Fig.2). Their internal arrangements share common motives due to the distinct geometry and intermolecular interactions, which reflect the peripheral atomic structure of PTCDA. Here, the main force driving the assembly stems from the attraction between the carbonyl oxygens and the hydrogen-termination along the sides of the perylene backbone, which orientates the nearest neighbors in the clusters to perpendicular
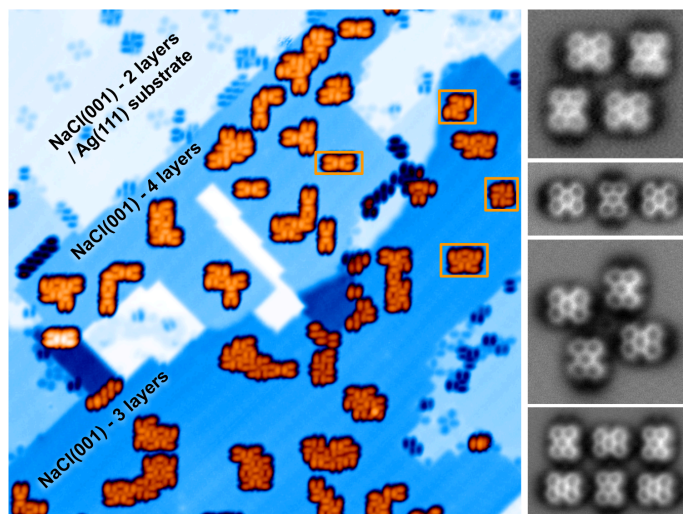

Fig.2: STM topography of aggregates, formed of PTCDA, adsorbed flat on NaCl on Ag(111) at 10K, and annealed to 80-120K. AFM images showing the PTCDA geometries are provided for the marked aggregates.

arrangements. Moreover, we found that the NaCl decoupling layer has a strong templating effect, pinning down the molecules to the lattice sites and imposing orientations on the molecule; the layer thickness also affects the types of aggregates formed.

These encouraging results open a large playground to steer specifically designed molecular precursors to form particular arrangements through careful choices of the chemical substituents and the annealing temperature, **to finely balance the directional anisotropy of the intermolecular interactions and tune the size of the aggregates**. In addition we envisage aggregate engineering by selection of the insulator material (NaCl, KCl, RbI, h-BN etc.) and the substrate termination (001, 111 and 110 planes of the Ag, Au crystals). We will exploit this potential in close cooperation with theoretical modelling. Molecular precursors with favourable optical properties will be identified through preselection by means of state-of-the-art computational techniques, such as density functional theory methods (DFT) and its time-dependent counterpart (TD-DFT). Their ground and excited states energy and optical response (i.e. transition dipole moments) will be determined, along with their evolution upon aggregation. A computational approach will also be devised in order to account for the effects of the thin insulating layer on the aggregate geometry, its electronic configuration and the photophysical properties.

Well-geometrically and electronically characterized clusters are the prerequisite for investigation of their excitonic properties from the point of view of their potential implementation as quantum-logic gates, which we are going to probe at the second stage of the experimental effort. Inspired by the recent advances in STML, **we have recently implemented an experimental optical detection line into the UHV AFM/STM with picosecond time-resolution** capabilities in our laboratory. Up to our knowledge, this is still the only example of such functional combination that simultaneously gives luminescence spectra with submolecular resolution and can directly correlate them with the AFM images, their frontier orbital symmetries and their energetics. We are using a grating-type spectrograph equipped with a cooled CCD to detect luminescence of single-molecule emitters or the aggregates. We have implemented a series of upgrades that permit to record the spectra in fast sequences, allowing hyperspectral mapping of the optically active objects of interest[55] and we can direct part of the photons to an avalanche photo-detector for time-resolved experiments.[57]

Examples of our most recent combined geometrical, electronic and spectral characterization of a PTCDA monomer and a trimer is presented in Fig.3. It shows the backbone atomic structures of the molecules, and thus the precise geometry of the single molecules in the trimer. The tunneling

current images provide a view of the highest occupied orbitals. The near-infrared part of the spectrum taken over the monomer shows a sharp emission peak from an excited state of the PTCDA, whose intensity can be mapped over the molecule to obtain the spatial distribution of the emission from the nanocavity. In the trimer, the emission fingerprint is composed of two peaks, each one dominating at a different location in the aggregate. The two photon maps at the energies corresponding to the peaks show a very distinct spatial distribution of the emission over the trimer, which is **a clear hallmark of the exciton delocalization and entanglement**. This preliminary result demonstrates the capability of the combined AFM/STM/STML to bring the proposed systems to their excited states and to resolve the delocalized excitonic states of an aggregate by probing them with an optical nanocavity.[27]
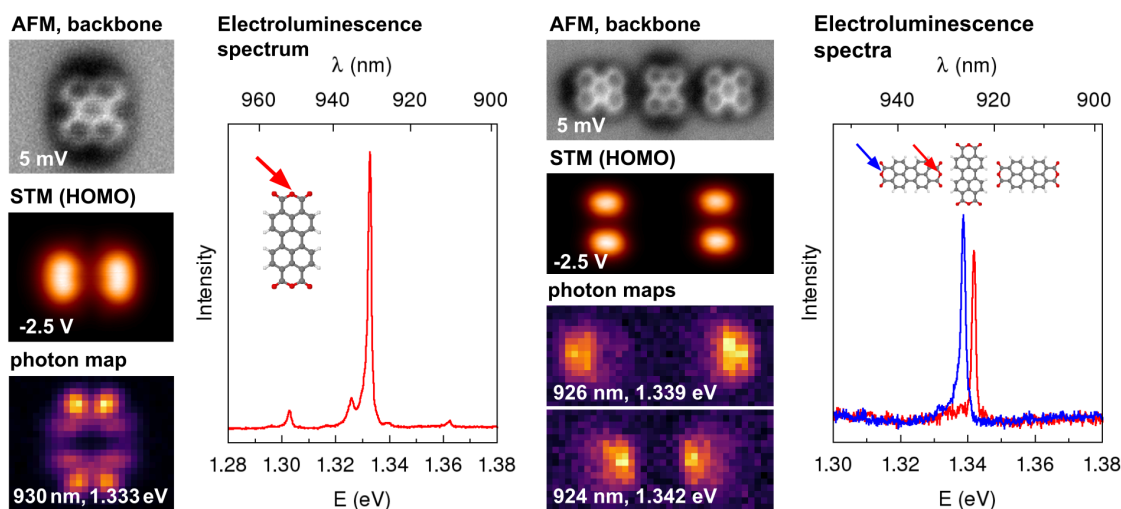

Fig.3: Combined AFM/STM/luminescence characterization of PTCDA monomer (left) and trimer (right). The arrows in the insets mark particular locations on the molecule where the plotted spectra were taken.

We aim to develop an **integrated simulation software to streamline a theoretical description of STML** experiment of self-assembled molecular aggregates on insulating substrates, with consideration of a realistic structure of SPM tips that determine the electromagnetic field in the optical cavity. The tool will utilize inputs obtained from TD-DFT calculations conducted on the electronic structure of entire aggregates or, alternatively, on individual constituent molecules and projecting the results onto more complex structures on substrate. The latter approach is essential since the direct treatment of large structures by TDDFT methods is currently beyond available computational possibilities. The implementation of the simulation framework will be composed of two segments: **i) versatile photon map generator** permitting to account for various nanocavity parameters and STM-current and **ii) the exciton model solver**, parametrized by the results of *ab-initio* calculations. The tool shall be a well-accessible program (e.g. a python module), to provide a general and user-friendly software for other experimental and theoretical groups. Such a tool will be first of its kind dedicated to the emerging field of STML.

The proposed approach to the realization of molecular quantum-entangled excitonic states by a synergy of on-surface molecular assembly strategies, optical UHV SPM instrumentation and advanced multiscale theoretical framework will open the possibility to perform unprecedented research that is not feasible with the present state of methodology. **We expect to reveal the fundamental relations governing the properties of excitonic entanglement in 2D aggregates of organic chromophores,** that can potentially permit designing and testing functional concepts of excitonic quantum-computing gates and networks.

OBJECTIVES AND METHODOLOGY

This project's **ultimate goal is to devise first-generation model quantum excitonic circuits**, constructed as aggregates of promising molecular precursors. The primary target of the exploration will be the photophysics of molecular aggregates with confined dimensionality, involving

delocalization and evolution of the excited states within a plasmonic nanocavity (WP1, WP2). For these purposes we will employ the ground-breaking methodology of real-space subnanometer mapping and picosecond real-time spectroscopy. We will pursue a deep understanding of the fundamental phenomena governing such entangled excitonic nanosystems and the emerging quantum manifestations. In the WP3, we plan to identify and develop a suitable theoretical framework to correctly describe newly formed aggregates. Indispensable part of this endeavor will be to develop a bridge between the cutting-edge experiment and the state-of-the-art theory, with a custom framework for the simulation of the bidimensional aggregates and their photonic maps.

Work package 1: Creation of nanoscale molecular exciton aggregates. This work package will be dedicated to the task of forming small aggregates of electronically addressable, optically active molecular species manifesting entangled excitonic states for further investigation in WP2. We will first **perform a screening of the molecular precursors** with planar backbones, checking their suitability for construction of tailored bidimensional aggregates on the thin insulating layers, taking into account their coordination properties as geometrical shape and presence of functional groups (e.g. carbonyl, amine or sulfanyl). This will be a joint task between theory and experiments. In particular, in the theoretical part of this task, we will attempt to **predict the relevant properties of the excited states (energy and transition dipole moments) based on the *ab-initio* calculations.** In the experiment, for each particular species, after finding the correct deposition parameters, we will perform a detailed AFM/STM characterization, using CO-functionalized tips. Subsequently, we will **verify their photophysical properties by the STM-induced electroluminescence** measurements.
For the molecular candidates that will finally prove successful experimentally, we will **adapt thermal and mechanical strategies to engineer aggregation** into clusters consisting of 1-20 units. In the thermal strategy, the substrates with the precursors will be annealed to temperatures in the 50-150K range and the cluster morphology and electronic properties will undergo an inspection by the AFM/STM methodology. Also, using the mechanical approach, we will move individual molecules together by manipulation with the tip and probe them in the same manner as the thermally formed clusters. These two strategies are complementary since they allow to form a large selection of clusters stable at cryogenic temperatures, as well as clusters that are otherwise thermodynamically unfavorable yet interesting to study (as e.g. clusters of species with large internal charge redistribution that induces anisotropic intermolecular Coulomb repulsion). In WP1, we will also explore formation of hybrid aggregates made from optically active molecules and spacers designed to be inactive or to mediate energy funnelling in the excitonic circuit.[84]

Work package 2: Experimental photophysics of bidimensional molecular aggregates. Clusters formed in the WP1, after verification of electroluminescence, will be a subject of a systematic study in this work package. First, we will take spatially resolved electroluminescence spectra on clusters consisting of a few molecular units. The particular focus will be on the hallmarks of the exciton delocalization and energetics, manifested as energy splitting of the main emission lines, corresponding to individual exciton modes. We will **take hyperspectral electroluminescence maps of the aggregates** mostly with metallic and CO-functionalized tips to resolve the spatial distribution of the emission for each exciton mode and analyze them in comparison to the results obtained using the theoretical framework created within the WP3. We will **attempt to track the exciton temporal evolution with phase fluorometry** and other time-resolved schemes (e.g. Hanbury Brown-Twiss interferometry), as a function of the exciton eigenmode wavelength and of external applied electrical fields. If the spectral, spatial and temporal resolution will be feasible, we will proceed to larger clusters, adopting an analogous experimental approach and analysis method.

Work package 3: Entangled excitons - bridging the experiment and theory. We will bridge the gap between the experimental data and the theoretical description by creating an algorithm for simulations of the STM photon images and their spectral properties. It will be based on *ab-initio* calculations and simplified models accounting for the general principles that govern the exciton-exciton interaction in bidimensional molecular aggregates that lead to the entanglement

phenomena at the root of the submolecular contrast in the photon maps. The tool will consist of two submodules: **(i) photon-map simulator and (ii) solver for the exciton model**. (i) The photon-map simulator will be an application of a previously showcased method[71] where the optical field in a tip-induced plasmonic cavity is coupled with the transition density of the molecular exciton. We will optimize the numerical efficiency of the method, and allow a more general shape of the cavity created by an arbitrary experimental tip, including the effect of flexible-particle terminations of the probes (e.g. CO-passivated tips). The algorithm will be based on discrete convolution, which can be calculated efficiently by fast fourier transform (FFT), a strategy we used for simulation of AFM/STM images in the framework of the ProbeParticle model.[85,86] Finally, we shall compare the character and shape of the experimental hyperspectral data to the simulations performed using our framework. The complete program will be made publicly available through popular code-sharing platforms (e.g. GitHub).

In the solver (ii), a model exciton Hamiltonian will be set up for the aggregates, and parameterized based on *ab-initio* calculations. In particular, the on-site energies of the constituent molecules will be supplied from TD-DFT calculations, and the relevant intermolecular interactions (i.e. exciton couplings) will be calculated by grid-integration from the electronic structure (transition densities) of individual molecules. The grid approach goes beyond the dipole-dipole approximation and allows a straightforward implementation of other relevant intermolecular interactions (e.g. exchange or charge transfer couplings). Our tests have shown that good estimates of the coupling for arbitrary orientation of molecules can be obtained very efficiently (< 1s on a normal pc). This strategy allows to examine many aggregate structures of large dimension, avoiding costly *ab-initio* calculations.

Year	2022				2023				2024			
WP1: Creation of exciton aggregates	■	■	■	■	■	■	■					
molecule preselection exp.+theory	■	■	■	■								
aggregation strategies				■	■	■	■					
WP2: Photophysics of aggregates						■	■	■	■	■	■	■
mapping of exciton delocalization						■	■	■				
tracking of the exciton evolution								■	■	■	■	■
WP3: Theoretical bridge			■	■	■	■	■	■	■	■	■	■
photon map simulator			■	■	■	■	■					
exciton model solver						■	■	■	■	■	■	■

Table. 1: Time flow of the work packages

Impact. i) new perspectives in selection, assembly and harnessing of molecules for progressive optical applications; ii) theoretical framework to simulate the experimental exciton maps, taking the step forward to design first-generation quantum networks from individual excitonic constituents with custom functionality

We plan to disseminate and discuss the results in the international community using high-impact international journals and dedicated international conferences or consulting external specialists. It is understood that we should be able to recognize, process and publish any significant discoveries which will emerge as a result of this research.

The team. To fulfil the particular objectives I will use my full scientific and leadership experience, especially my practical knowledge of the photon-STM methodology, with a commitment of 50%. I will participate in the experiments, data analysis and the software development. **One post-doc (R.F.)** will be hired for the experimental work. The **second theoretical post-doc (S.C.)** will be hired for the **TD-DFT calculations**, which are crucial for the correct implementation of the semiclassical model and deeper understanding of the exciton entanglement phenomena. The implementation of the model **will be overseen by P. H.** He is extremely skilled in high-performance molecular and atomistic simulations of images from scanning probe microscopy that combine classical and quantum approaches, such as the successful Probe-Particle simulation software package.[87] Involvement of **one student** is planned for the duration of the project with the purpose to provide a platform for their **PhD thesis** in experimental physics. Any recruitment will be performed in accord with the established institutional protocols (EC HR Excellence in Research).

We have an ongoing **very fruitful collaboration with Dr. Pablo Merino** from the Instituto de Ciencia de Materiales de Madrid in Spain, who is an expert in experimental STML and the related field. We plan to include him in the design of the experiments, discussion of the data and writing of the manuscripts.

Instrumentation. The major part of the experimental work will rely on a **fully consolidated hybrid UHV photon-RF-AFM/STM** system (Createc, GmbH., 2018). It is equipped for preparation of the samples in-situ, including ion sputtering, annealing and molecular deposition, possible either on samples at room temperature or directly inside the head. The scanning head of the microscope is equipped with an optical access and a high-aperture aspherical lens aligned with its focal plane in the proximity of the tip-sample junction. That allows an efficient coupling of the emitted photons from/to an external detection pathway through a set of viewports. A dedicated **highly sensitive CCD spectrograph** is employed for full spectroscopic characterization of the collected photon beam and **single-photon avalanche photodiodes** are used for the picosecond light spectroscopy. Radio-frequency line has been recently added to the system to enable electronic excitation in the **1-20 GHz range**. The control electronics of the microscope is the most-advanced on the market (Specs GmbH. Nanonis), allowing various modes of multichannel data acquisition and full automation of the measurements *via a programming interface*. The cryogenic liquids and other essential infrastructure necessary for uninterrupted operation of the instrument are available at the Institute. Molecules unavailable commercially will be synthesized on-demand externally.

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