Proposal Title: Hybrid Organic-Inorganic Microcavities in a Light Emitting Diode Design

Application Reference Nº: 4317

1) Purpose of the visit

Design, fabrication and investigation of strongly coupled hybrid organic-inorganic microcavity light emitting diodes via photoluminescence and electroluminescence spectroscopy.

2) Description of the work carried out during the visit

Prior sample fabrication, an extensive and detailed simulation of the complex microcavity structure was pursed by means of the transfer matrix method. The code implemented for the purpose permits to calculate the electromagnetic mode across the mutilayer stack based on the refractive index of each layer. This allows any planar microcavity (MC) system to be reproduced under illumination of a light source at fixed energy and angle of incidence. The transfer matrix method also permits to extract the field antinode position and tailor accordingly the layers thickness to match the required conditions for the achievement of strong coupling.

Molecular beam epitaxy growth of the bottom half III-V inorganic cavity followed: bottom *n*+ doped Distributed Bragg Reflector (DBR) mirror, 2 sets of 3 GaAs/AlGaAs quantum wells and *p*+ doped AlGaAs spacer/injection layer. Spin casting of the J-aggregate dye solution was performed at the Nanofabrication Centre at the University of Southampton while top DBR deposition carried by the Helia Photonics company. Here, both *p* and *n* type doped layers guarantee the efficient injection of carriers in the quantum wells from the two metallic contacts. The top one deposited via gold evaporation while the bottom obtained by positioning the final device onto an electrically connected mount. Besides, etching was performed to ensure electrical isolation and avoid that the injected carriers would spread horizontally under the top contact. With this process we obtained different size mesas (diameter of 200, 350 and 500 μm) which forced and localized the electrical injection on a small active area. Reflectance of DBR mirrors, quantum wells and J-aggregate emission energy, together with layer thicknesses, were characterized at each step of the fabrication process to assure quality and accuracy of all the components of the structure.

As first step after the completion of the device, design and realization of the optical setup (figure 1) was attained by exploiting and combining the ultra-fast laser system facilities and the strong expertise of the Microelectronics Research Group in the characterization of optoelectronic devices. Specifically, the setup consists in a collection system which allows for angle resolved spectroscopy of the microcavity sample photoluminscence (PL)/electroluminescence (EL) by energy resolving and subsequently imaging the Fourier plane of the emitted signal on a Charged-Coupled Device (CCD). During the entire stay slight modifications of the setup were accomplished to follow the different type of analysis required: PL under non-resonant pumping (1.65 eV at 80 MHz repetition rate), power dependence measurements following near-resonant excitation (1.59 eV at 100 kHz repetition rate) and at last EL spectroscopy by means of a DC voltage generator. Furthermore, fabrication and processing facilities have been used to repair the electrical contacts of the MC LEDs to assure in this way continuative sample operation. Following the optical characterization, direct interpretation of the experimental results has been performed with the help of a coupled harmonic oscillator model. Simulations and related discussions which have been very fruitful and accurate in the explanation of the measured data, were accomplished based on a day to day interaction with Prof. Pavlos Savvidis and Dr. Simeon Tsintzos.

The high scientific level of the obtained results led to the realization of a manuscript, now under revision, to be submitted to high impact factor journal. The results have also been presented at the International Conference on Optics of Excitons in Confined Systems (OECS13) as oral talk.

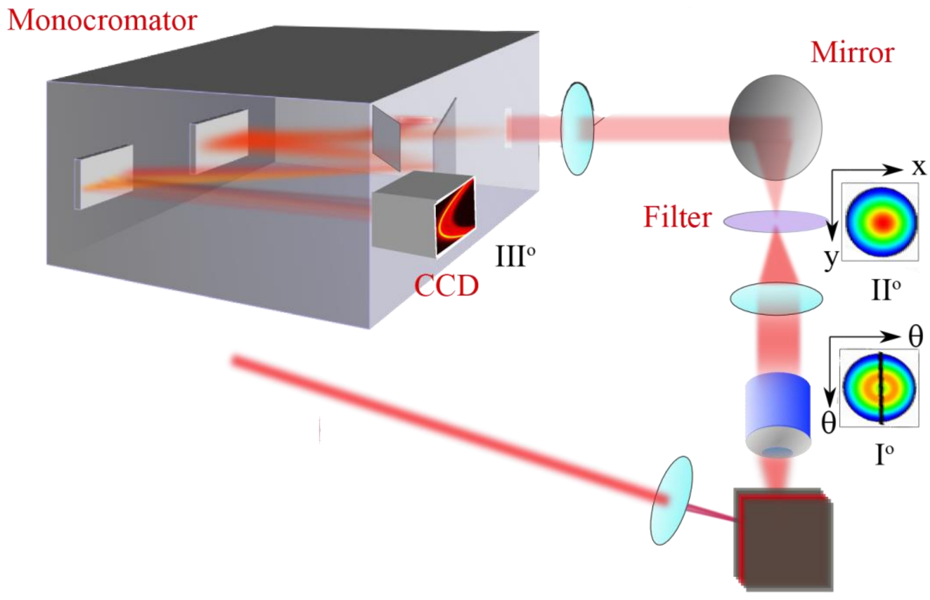

Figure 1: Schematic drawing of the experimental setup used for angle resolved photoluminescence/electroluminescence imaging. For guidance (I°, III°) Fourier plane (k-space) and (II°) real space dispersions are shown at the specific positions along the setup.

3) Description of the main results obtained

The optical characterization of the fabricated samples started with a preliminary investigation pursued on a microcavity structure modified with respect to the original design to incorporate only Wannier-Mott (W-M) inorganic excitons. The J-aggregate dye was removed from the organic solution which was spin coated to preserve the correct cavity thickness. This approach allowed the study of quantum wells exciton-photon coupling and the coupling strength (Rabi splitting) to be extracted. Upper and lower polariton dispersions were observed and their separation at the resonance point found to be 5 meV. This Rabi splitting value is in accordance with typical microcavities [1], similar in quality and composition to the one under investigation.

After this precursory study, the full hybrid microcavity LED was characterized. Starting from the investigation of angle resolved photoluminescence emission we could immediately ascertain the simultaneous strong coupling of both organic and inorganic excitons with the optical cavity mode. The presence of strong coupling regime, which results in the formation of hybridized polariton states, is suggested by the appearance of a polariton branch (LP), spectrally separated from the J-aggregate energy and which exhibit characteristic anticrossing behaviour. A further confirmation was provided by theoretical fitting of the experimental data using a coupled harmonic oscillator model (figure 2 **a**).

Frenkel exciton Rabi splitting was extracted and its value (60 meV) found in agreement with the high oscillator strength possessed by organic J-aggregate cyanine dyes [2]. The model also permitted to study the fractional weight of all components in the polariton particles and hence provide the understanding of the relaxation/population mechanisms of the polariton branch states. This has been possible by extraction of the Hopfield coefficients shown in figure 2 **b**. The polariton's (Frenkel and W-M) excitonic and photonic fractions at each wavevector control the luminescence and relaxation processes along the branch. Furthermore, the excitonic components are also responsible for the mutual polariton-polariton interaction which defines the nonlinear properties.

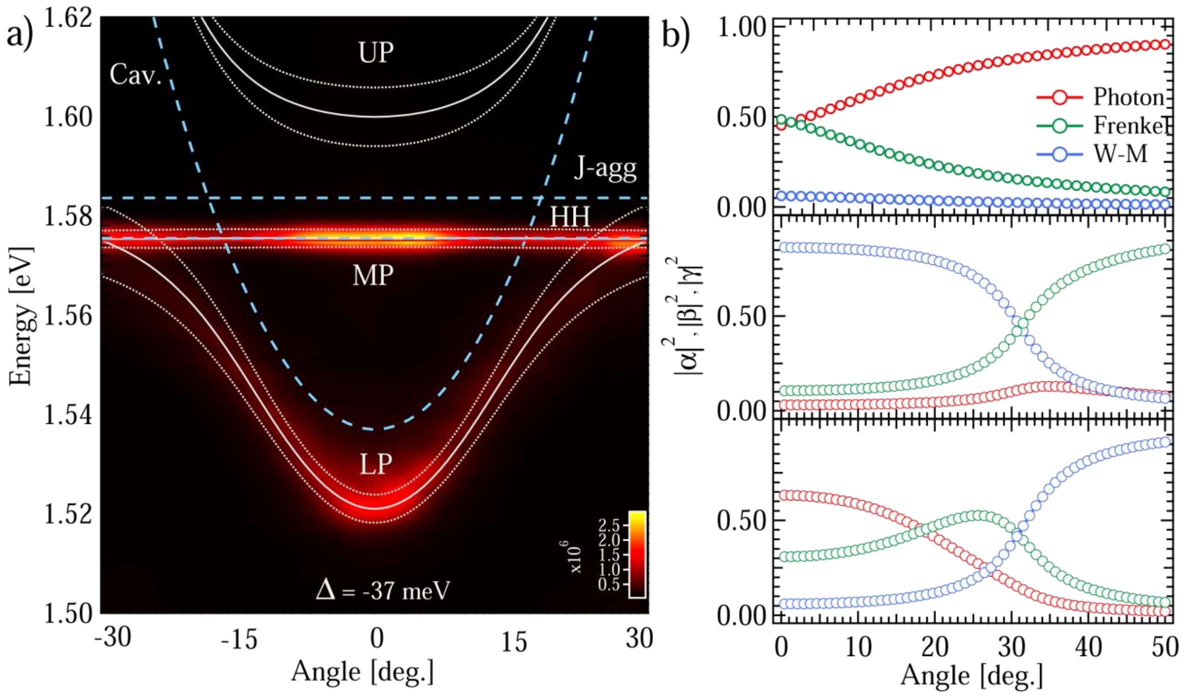

Figure 2: a) Photoluminescence imaging of the hybrid sample at cavity detuning of -37 meV. Blue dotted lines refer to excitons and cavity positions while the white lines to the polariton dispersions and related bandwidth. Here cavity detuning (Δ) is defined as difference between optical mode position and heavy holes (HH) energy at *k*=0. b) Hopfield coefficients for upper, middle and lower polariton branches as extracted from the couple oscillator matrix.

From such analysis it was found that, out of the upper, middle and lower branch, the latter is the one that appears to carry the strongest mixing of all the three components (figure 2 **b**). Specifically it was quite surprising to notice the occurrence of such high level of hybridization also at the bottom of the dispersion (zero wavevectors, *k*=0) where macroscopic population and related cooperative phenomena are expected to occur. The simultaneous presence of not negligible photon, Wannier-Mott and Frenkel fractions is expected to enhance photoluminescence, particles nonlinearities and at the same time favour the occupation of such lower polariton states through efficient vibrationally assisted polariton scattering, important process occurring in organic based MCs [3]. Most remarkable is the fact that such particular mixing can be easily modified by cavity detuning variation, being possible simply by investigation of different locations along the sample. The spin casting process, which intrinsically provides approximately 5/10 nm gradient to the resulting thin film thickness, allows in fact for a cavity shift of about 33 meV. Precisely from such cavity detuning investigation, responsible for strong modification of the polariton features, we could experimentally observe a negative inflection of the middle polariton dispersion for a detuning value of Δ=-22 meV. This peculiar phenomena was found to occur at the wavevector position where polaritons possess equal Frenkel and W-M percentages and understood as due uniquely to the simultaneous coupling of these two completely different excitonic species which possess highly contrasting oscillator strength and broadening of the exciton line. On that specific region, the decrease of the polariton energy with increasing momenta, implies negative wave packet group velocity ($v_g = \partial\omega/\partial k$) which at last results in negative refraction of light. At the inflection point, where polariton mass is negative ($M = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2}\right)^{-1} < 0$), we also expect strong polarito-polariton repulsive interaction [4]. The combination of these effects provides the most favourable condition for the observation of parametric scattering, solitonic features and other nonlinear phenomena.

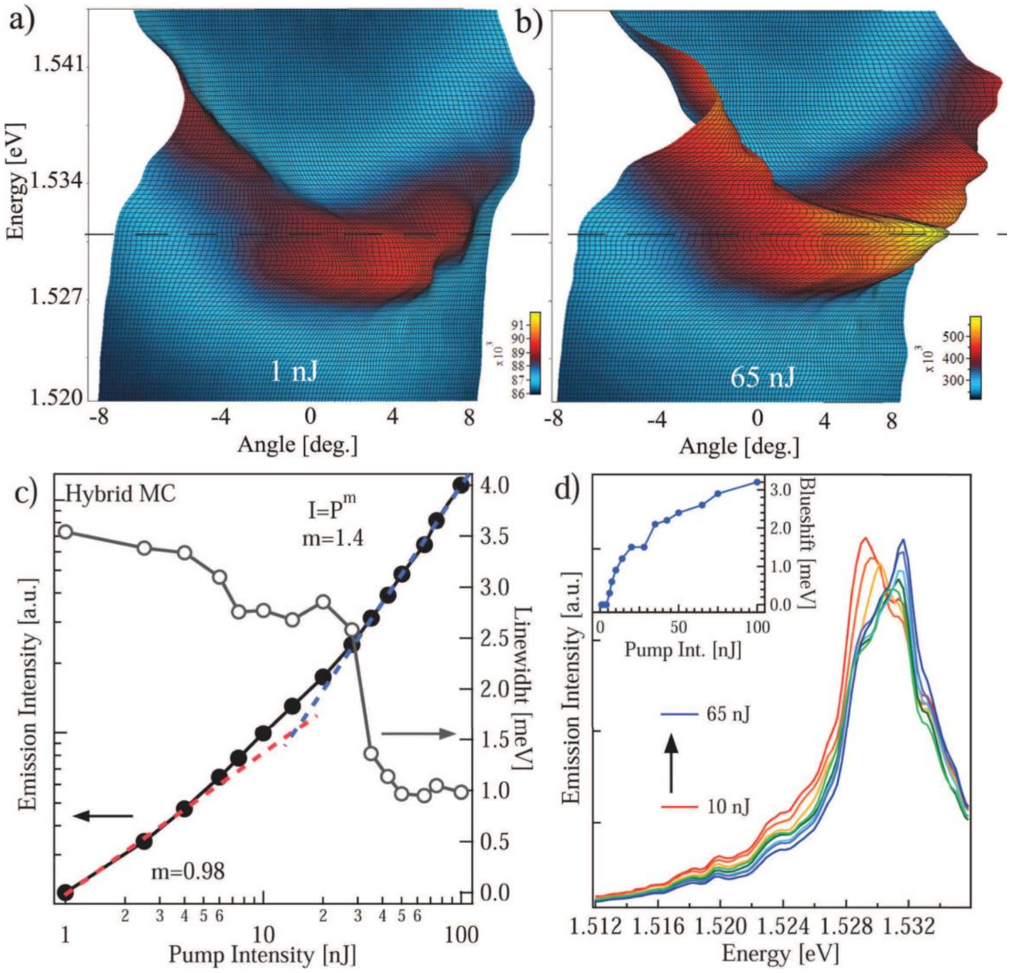

Figure 3: a, b) LP photoluminescence images of the hybrid system at 1 nJ and 65 nJ pump energies. Related profile spectra, normalized to the relative applied power, are shown in (d); related peak position shift is also displayed as inset. c) Emission intensity of the lower polariton branch at k=0 (black dots) and spectral narrowing (grey circles) as function of excitation energy.

The following step consisted in the investigation of nonlinear polariton photoluminescence emission properties. A low repetition rate (100 kHz) pulse beam was used to pump the system while the photoluminescence signal was collected through the setup described above. Even if clear lasing threshold behaviour was not achieved, we identified a superlinear dependence of the PL intensity with the excitation energy. Specifically we found a curve slope m of 1.4 which follows the initial linear regime (*m*=1) from the transition pump energy of 28 nJ (figure 3 **c**). As can be seen from the dispersion images of the lower branch displayed in panels **a** and **b** of figure 3, as the pump power increases the exciton-polariton population, initially extended on a broad range of states, gradually blueshifts (3 meV) and condenses to form a sharp peak located at the high energy side of the emission spectra. Furthermore, spectral narrowing of the PL emission at *k*=0 (2.5 meV) suggests the build-up of coherence in the system.

Although Bose-Einstein condensation of exciton-polariton has been observed in inorganic MCs, we conjecture that condensation of Frenkel excitons, only theoretically predicted [5], is here limited by bimolecular quenching. This constraining mechanism frequently occurs in a big variety of molecular compounds and can become very effective in a microcavity system excited by a non-resonant optical pump. In that case in fact, the main part of the excitation is concentrated in incoherent states (the exciton reservoir) which possess high probability to annihilate and decay nonradiatively. Despite this limitation, our experiment suggests that the unique mixture of properties of organic and inorganics compounds, achieved by photon mediated hybridization, is responsible for the observed superlinear emission which has to be considered as a pre-lasing regime that anticipates macroscopic polariton condensation.

This conclusion is experimentally supported by direct measurement of LP photoluminescence of two different microcavity structures with very similar quality factors but which separately incorporate only organic and inorganic excitons. By assuming identical excitation conditions, these systems did not show any nonlinear response. For both structures in fact, LP emission intensity showed a linear and subsequent sublinear increase with the excitation power indicating saturation of emission. This behaviour, in case of the organic sample, is caused by the loss of strong coupling due to photobleaching of the J-aggregate dye. The observed PL linewidth broadening and redshift of the peak maxima confirm the loss of strong coupling regime. These comparative measurements stress the advantage of mixing organic and inorganic materials to overcome the intrinsic limitations imposed individually by each component. Additional calculation of the nonlinear contribution provided by Frenkel and Wannier-Mott excitons to the final hybridized polariton particles have shown that even a small fraction (Hopfield coefficients) of the W-M component could strongly enhance their nonlinear character and justify in this way our experimental findings. This consideration is based on the magnitude of the organic and inorganic polariton nonlinear interaction terms, calculated considering the measured Rabi splitting values and the intrinsic excitonic size [6]. Specifically, the inorganic exciton term was found to be 8 times bigger with respect to the Frenkel counterpart despite the higher percentage of the latter in the final polariton states.

The full potential of the proposed organic-inorganic system is evaluated further by the experimental observation of photon mediated exciton mixing via electrical injection. Due to the particular structural design implemented here, high electrical conductivity typical of inorganic semiconductors is exploited in combination with the strong optical response (oscillator strength) of the organic counterpart. As such, efficient intracavity injection of carriers in the quantum well layers allows for the created excitation to be shared among the three polariton branches as resulting from the exciton-photon coupling regime. In the same way as in the optical case, the couple harmonic oscillator was used to fit the experimental curves. By implementing the previously obtained values of Frenkel and W-M Rabi splitting high level of precision was attained thus underlining that the electrical excitation still maintains the light-matter interaction strength. As consequence, hybrid polariton nonlinear properties previously observed are expected to be preserved.

An additional advantage accomplished by the exploitation of an intracavity pumping scheme is directly referred to the reduction of the quenching process previously introduced which relates to the intrinsic disorder and inhomogeneousity caused by the J-aggregate compound. When optically pumped in fact, the formation of highly populated and uncoupled Frenkel exciton reservoir states can cause important losses and hence reduce the overall polariton population. By direct intracavity excitation, the formation of such reservoir is prevented since the entire excitonic population is transferred to polariton states. Suppression of nonradiative decay and recombination of uncoupled excitons could therefore guarantee large polariton densities.

For a general evaluation of the figure of merit of such device we measured the diode turn on voltage (2.5 V at 20 Kelvin) and extract a corresponding polariton density value n of approximately 2.3×10^{9} cm^{-2} ($n=J\tau/e$ where J is the current density, τ the average carrier lifetime, 500 ps, and e the electron charge). This relatively small value has to be reconsidered by taking into account the very weak turn on voltage attained here, compared to previously reported values related to inorganic and organic based LEDs [7, 8]. In fact, for a saturation current value of 10 mA, measured for a weakly coupled test sample, population density is expected to increase up to 2 orders of magnitude. Such analysis was not directly performed due to the sensibility of the organic dye to the heat provided by such current values. Preliminary electrical tests on the bare J-aggregate thin film are thus required to verify the effects of intense applied voltages which can in fact irremediable damage the molecular structure and alter the working function of the device.

Besides, we believe that the realization of a hybrid microcavity device which enhances polariton nonlinearities, sustains strong coupling regime even under electrical excitation and furthermore provides a very flexible platform for the investigation of the Bosonic properties of exciton-polaritons, opens up a concrete alternative route to traditional microcavities (organic or inorganic) structures and at the same time provides new room for improvement towards the fabrication of functional polaritonic devices.

References

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4) Future collaboration with host institution (if applicable)

The observation of middle polariton dispersion inflection represents an important achievement due to the high potential presented by the peculiar features possessed by polariton states at such defined position. As explained previously, the particular conditions observed (negative refraction) suggest the presence of high polariton population densities which possess strong nonlinearities due to polariton-polariton mutual interaction. For this reason ad hoc optical experiments can be designed and pursued for the specific investigation of nonlinear phenomena. Double beam spectroscopy would in fact permit the study polariton propagation and parametric scattering as well as bright/dark soliton formation. One additional advantage is provided by the high accessibility of these states compared to the experimental difficulties presented by the fine searching of the inflection point on the lower polariton branch, implied for such kind of analysis on traditional microcavities. Our system would permit a simplification of the experimental setup and especially facilitate the observation of the mentioned effects.

It is worth mentioning that the eventual achievement of positive results would be of a high scientific impact due to the novelty of the research goals which could permit to corroborate the scarce knowledge on the Bosonic features of Frenkel type polaritons by proving experimental evidences of cooperative phenomena. The realization of the mentioned experiments is still under planning but considered to take place in the MRG laboratories under the supervision of Prof. P. Savvidis within the following months.

5) Project publications/articles resulting or to result from the grant

"*Superlinear Polariton Emission of Hybrid Organic-Inorganic Microcavities.*"
Niccolo Somaschi, Simos Tsintzos, Dave Coles, David G. Lidzey, Zacharia Hatzopoulos, Pavlos G. Lagoudakis and Pavlos G. Savvidis. UNPUBLISHED.

6) Other comments (if any)