Temperature dependent polariton emission from strongly coupled organic semiconductor microcavities

Samira Ceccarelli, Jakub Wenus, Maurice S. Skolnick and David G. Lidzey*

Department of Physics and Astronomy, The University of Sheffield, Hicks Building, Hounsfield Road, Sheffield S3 7RH, United Kingdom

*Author for correspondence: e-mail d.g.lidzey@sheffield.ac.uk, Phone: +44 (0) 114 222 3501, Fax: +44 (0) 114 222 3555

Abstract. We investigated the absorption and photoluminescence (PL) of J-aggregates of a cyanine dye both in a thin film format and when used as the active layer in a strong-coupled microcavity. We show that as temperature is reduced, the absorption linewidth of the J-aggregates narrows and shifts to higher energy. When the J-aggregate is placed in a microcavity we find that the energy of the polariton modes also shifts to higher energies as temperature is reduced. We compare the intensity of PL emission from the upper and lower branches at resonance as a function of temperature, and find that it can be described by an activation energy of 25 meV. PL emission spectra at resonance also suggest that uncoupled excitons inside the microcavity populate the upper polariton branch states.

Keywords: Strong coupling, exciton, organic microcavities, J-aggregates, absorbance, photoluminescence, reflectivity, temperature dependence.

Introduction. Strong-coupling can be achieved at room temperature in microcavities containing organic semiconductors due to the enhanced binding energy of Frenkel excitons. Apart from one recent study [1], most work on this topic has been restricted to room-temperature measurements [2, 3]. In this paper, we characterize the photoluminescence emission (PL) from microcavities containing J-aggregates of a cyanine dye at temperatures between 80 K and 300 K and show evidence of the population of the upper polariton branch from uncoupled excitons.

Experimental methods. In the top left corner of Fig. 1a we show the chemical structure of the cyanine dye F1 used in the experiment. This material has been characterised in thin-film format [4] and when incorporated into a microcavity [5, 6]. For control optical measurements, the dye was dissolved in a water-based gelatine solution and spin-coated on a glass substrate. To fabricate microcavities, the F1 dye/gelatine solution was spin-cast onto a DBR (consisting of 9 pairs of SiN/SiO_2) grown by plasma enhanced chemical vapour deposition (PECVD) on a quartz substrate. A top silver mirror was then deposited onto the organic layer by thermal evaporation. This formed microcavity

structures having a Q-factor of 70. Samples were mounted in a nitrogen-cryostat and characterized between 80 K and 300 K. PL was generated from each structure using either a GaN laser emitting at 405 nm with a power of 2.5 mW or a He-Cd laser emitting at 442 nm.

Results and discussion. Fig. 1a shows the absorbance and PL of J-aggregates of dye F1 measured at 300 K. The J-aggregates absorb and emit at around 590 nm (2.1 eV). Both absorbance and PL spectra have linewidth of around 35 meV with a Stokes shift of 4 meV between absorption and emission. As the ambient temperature is reduced to 80 K, the absorbance and PL both shift to higher energies as shown in Fig. 1b. This energy-shift is accompanied by a narrowing of the absorption and emission linewidth.

Figure 2a shows the results of angle-resolved reflectivity measurements on microcavities containing dye F1. Here, reflectivity spectra were recorded at 300 K for various external-viewing angles between 25º and 50º. It can be seen that the cavity undergoes anti-crossing around the peak J-aggregate absorption energy, demonstrating that it operates in the strong-coupling regime. Exciton-photon resonance occurs at 35º (where polariton branches have a minimum energy separation) and corresponds to a Rabi-splitting energy of 130 meV. Angle resolved PL spectra recorded at 300 K are shown in Fig. 2b. The spectrum recorded at resonance is marked in bold. Here, we identify emission from both the upper polariton branch (UPB) and the lower polariton branch (LPB). We also highlight the emission from uncoupled excitons (Ex).

In Fig. 3a we show the dispersion curves obtained from angle resolved reflectivity measurements at 80 K, 200 K and 300 K. In the same figure we plot dispersion curves calculated on the basis of a two-level model. It can be seen that at all temperatures, anticrossing is observed between the UPB and LPB. We note that the Rabi-splitting energy does not change appreciably indicating that the J-aggregate oscillator strength remains approximately constant as a function of temperature. It can

be seen however that the dispersion curves shift to higher energy as the temperature is reduced. This energy shift is consistent with the temperature-dependent shift of the F1 aggregates: in particular, we observe the same 20 meV energy shift between 80 K and 300 K in the dispersion curves as is observed in the control films of F1 J-aggregates (see Fig. 1b).

In Fig. 3b we plot the emission from the cavity at resonance at 100 K and 300 K, with both spectra normalized to the intensity of the LPB. Emission from uncoupled excitons at 100 K can be clearly seen. The energy of the UPB and LPB approximately coincide with that measured in reflectivity (to within 20 meV). It can be seen that the UPB intensity reduces as temperature is reduced. In the figure inset, we make an Arrehnius plot of the ratio of upper to lower branch emission intensity against 1/KT. The data follow a straight line, having a gradient (equivalent to an activation energy) of 25 meV. This energy is close to the peak energy separation between the UPB and the uncoupled exciton energy, which are separated by 35 meV. Note that this agreement is further improved when we take into account that the uncoupled exciton and UPB have a linewidth (at 300 K) of 42 and 33 meV respectively. This suggests that the UPB is in part populated through scattering from uncoupled exciton states.

Conclusions We have measured the absorption and PL of J-aggregate excitons as a function of temperature both in control thin films and in a strong-coupled microcavity. We find that both the uncoupled excitons and the polariton modes show the same energy shift as the temperature is varied between 80 K and 300 K. The PL emission intensity from the upper and lower polariton branches recorded at resonance suggests that upper branch states are populated by uncoupled excitons.

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Figures captions.

Figure 1. a) Absorbance (solid line) and PL (dashed line) at 300 K of J-aggregates of cyanine dye F1 dispersed in gelatine matrix in a thin film spin-coated on a glass substrate. Top left corner: Chemical structure of dye F1. b) Energy shift of peak energy E_T at temperature T relative to peak energy E_{RT} at 300 K (left axis) and spectra linewidth (right axis) as a function of temperature for absorbance (open symbols) and PL emission (solid symbols).

Figure 2. a) Angle resolved reflectivity spectra at 300 K for microcavity containing J-aggregates of dye F1: the spectrum at resonance (i.e. 35º) has been marked with a thicker line. Dashed lines show the anticrossing behaviour of the polariton modes. b) Angle resolved PL spectra at 300 K: resonance spectrum at 35º is marked in bold.

Figure 3. a) Dispersion curves from angle resolved reflectivity measurements at temperature: 80 K, 200 K, 300 K. Symbols refer to experimental data, lines (dispersion curves and localised excitons) to theoretical two-level model results. b) PL spectra at 35º (resonance) at 100 K and 300 K: LPB, exciton and UPB energy for 100 K are marked. Inset: Arrhenius plot of ratio of upper to lower polariton branch emission intensity as a function of 1/KT: symbols refer to experimental data and dashed line is the best linear fit.

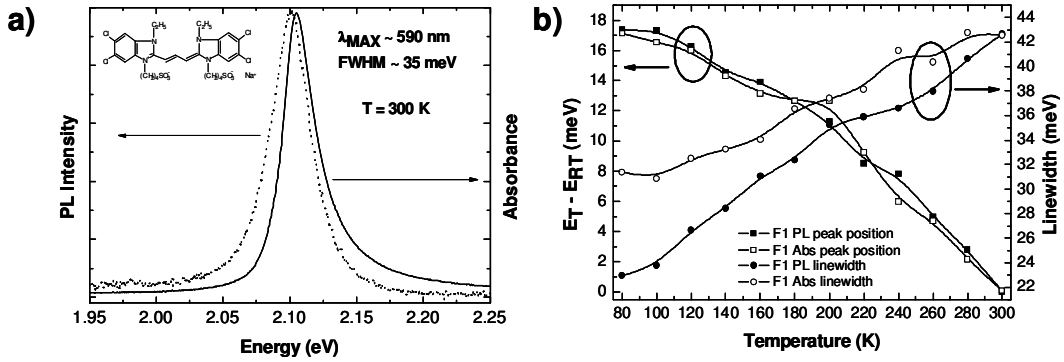

Fig. 1

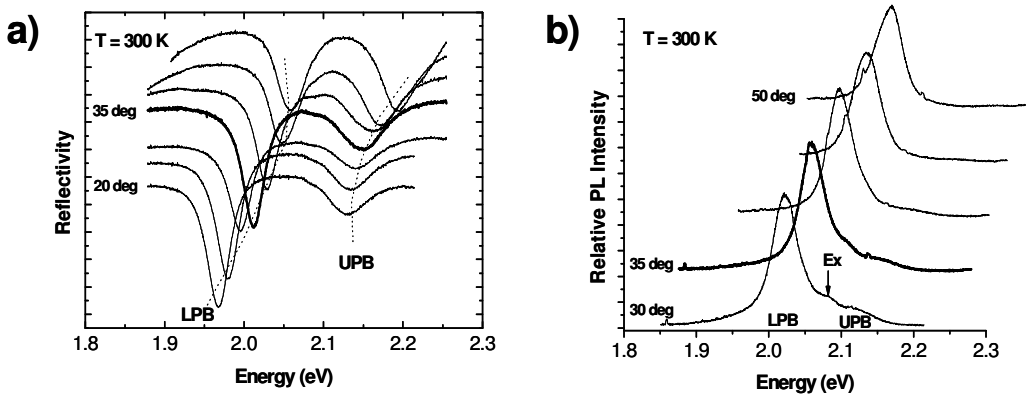

Fig. 2

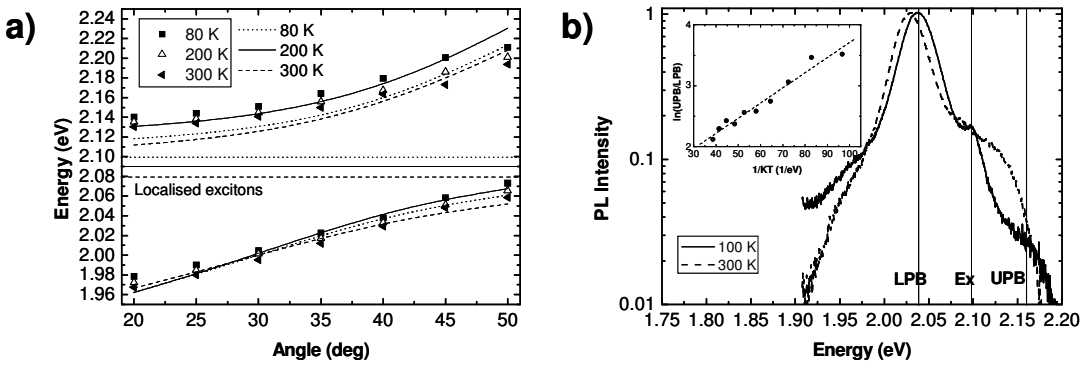

Fig. 3