

Amplified Emission in a Colloidal Photonic Crystal

L. González-Urbina, J. Pérez-Moreno, K. Clays

K. U. Leuven, Celestijnenlaan 200D bus 2425, B-3001 Heverlee, Belgium

The development of organic photovoltaics and OLEDs needs new manners to improve their low efficiency. One pathway recently opened is the use of sensitizers, either to harvest or to achieve the triplet excited states of the organic molecules. We demonstrate how the emission from Ir(ppy)₃, typically used as an emitter and as a sensitizer, is strongly enhanced in the presence of BA1q when affected by a photonic band gap. Since these organometallic compounds are extensively used in actual technologies, the results can have impact on many organic systems used in OLEDs and solar cells.

Introduction

Organic materials are of interest in light emitting technologies owing to their low price, low power operation and synthetic versatility. The physical process of organic light emitting devices (OLEDs) and organic photovoltaics (OPVs) differ slightly from their analogues based on inorganic materials. When a molecule is excited using an electrical stimulus, like in the case of light emitting diodes (LEDs), excitons are formed in both singlet and triplet states[1]. In the case of materials based on organic molecules the probability ratio for the generation of singlets and triplets in electroluminescence has been theoretically predicted to be around 1:3. Due to the conservation of the spin multiplicity, fluorescence is a process 75% less efficient than phosphorescence[2] but, unfortunately, phosphorescence in organic molecules at room temperature is not very common. Therefore, the internal quantum efficiency of a fluorescent organic molecule is theoretically limited to 25% which results in a reduce efficiency for OLEDs.

Sensitizers[3] are fluorescent or phosphorescent molecules used to improve the triplet quantum yield of the active layers in organic devices. They are normally doped in small amounts in the emitting layer of OLEDs and interact with the host molecules through fluorescence resonance energy transfer (FRET) processes. These molecules are used to improve the efficiency of OLEDs [4].

Concerning OPVs, efficiency is limited by the exciton diffusion length, which in turn is limited by the life time of the exciton. Life times are short for typically formed singlet states, while triplets have longer life times. The larger decay times of triplets grant the excitons longer diffusion length distances and therefore, it is possible to engineer thicker active layers which should lead to higher efficiencies. The advantage of using sensitizers in OPVs has been already proven[5]. *fac*-tris(2-phenylpyridine) iridium [Ir(ppy)₃] was used successfully to transfer the energy from the singlet excited state to the triplet state of N,N'-bis(phenyl)-benzidine (NPD), which is used in OPV as active material. The selection of the materials was made base on the energy of their excited states. Ir(ppy)₃ has shown also FRET[6] when combined with bis(2-methyl-8-quinolinato)-4-phenylphenolate aluminium (BA1q).

In our approach, we used this pair, Ir(ppy)₃ and BA1q (Figure 1), to study the Förster transfer enhancement when integrated in a colloidal photonic crystal (CPhC). To date, few reports have been published considering energy transfer processes in CPhCs[7]. In this work we demonstrate how the photonic band gap (PhBG) can be used to amplified the emission from a sensitizer. The anisotropic symmetry of colloidal crystals, packed in

a random hexagonal close packing fashion, imposes to these structures a twofold character when interacting with the light from a source embedded in the periodic medium, due to the angular dependence of the PhBG. On the one hand, the localization of light, similar to Anderson localization of electrons in solids, extends the lifetime of the excited states by suppressing the available energy levels at the PhBG energies, which increases the probability for resonant energy transfer and results in a population increase on the sensitizers excited states. On the other hand, the photons with energies corresponding to the band gap-edge travel with a reduced group velocity, which increases the probability of being reabsorbed by the acceptor molecules and leads to amplified emission.

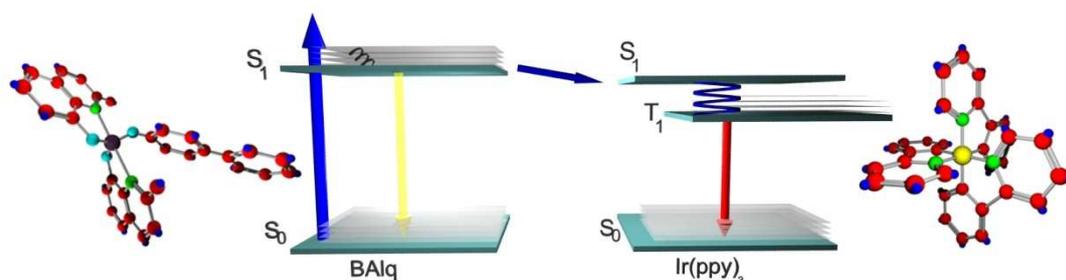


Figure 1. Representation of the energy levels from the BAQ (left) and Ir(ppy)₃ (right) and the Förster energy transfer process.

Since these organometallic compounds are extensively used in current technologies, the effect induced by the PhBG can have a highly beneficial impact on many organic systems used in OLEDs and OPVs.

Experimental part

In order to discern the effect merely from the photonic band gap and to discard any other environment effect the experiment will be performed for molecules hosted in exactly the same media. For this aim two photonic crystals are needed, one with the PhBG affecting the emission of the two molecules (called active crystal) and a second one with a PhBG acting far from their emission (called reference crystal). CPhCs were deposited by vertical deposition at 32° C from ethanolic suspensions. The reference crystal was used in order to have the same environment as in the active crystal but without the influence of the PhBG on the emission. CPhCs with random hexagonal close packing were obtained. All the glassware was cleaned with piranha acid (2/3 sulfuric acid, 1/3 hydrogen peroxide).

The extinction spectra of the photonic crystals (Figure 2-left) were measured using a Perkin-Elmer Lambda 900 UV-Vis NIR spectrophotometer. The reference CPhC stack had the PhBG at 385 nm and the active CPhC had it at 517 nm, measured at normal incidence.

The polymer films were deposited by spin coating (Specialty Coating Systems P-6712) on 13 mm diameter thin VWR Micro Cover Glasses (0.17 mm thick). The emission from the substrate was recorded to confirm that it is null or negligible for the experiments.

Each sample was prepared as follows. A doped film of poly (N-vinylcarbazole) (PVK), deposited by spin coating, was transferred on top of the PhC and, next, a second stack of CPhC was deposited. The PVK film contained different proportions of the two

molecules to be studied; 100% Ir(ppy)₃, 71.4% BA1q and 90.9% BA1q, in molar percent. The assemblage has been investigated at 80 and 300 K, using a Linkam cryostat cooled with Nitrogen. Excitation was achieved with a 325 nm Kimmon He-Cd laser. The power of the incident laser beam was 0.2 mW. The spectra were corrected using the response curve of this spectrometer obtained with a calibration lamp (Figure 2-right).

Sublimed grade Ir(ppy)₃ and BA1q and HPLC grade CHCl₃ were purchased from Sigma-Aldrich. PVK was purchased from ACROS Organics. These chemicals were used as received from the suppliers, without further purification.

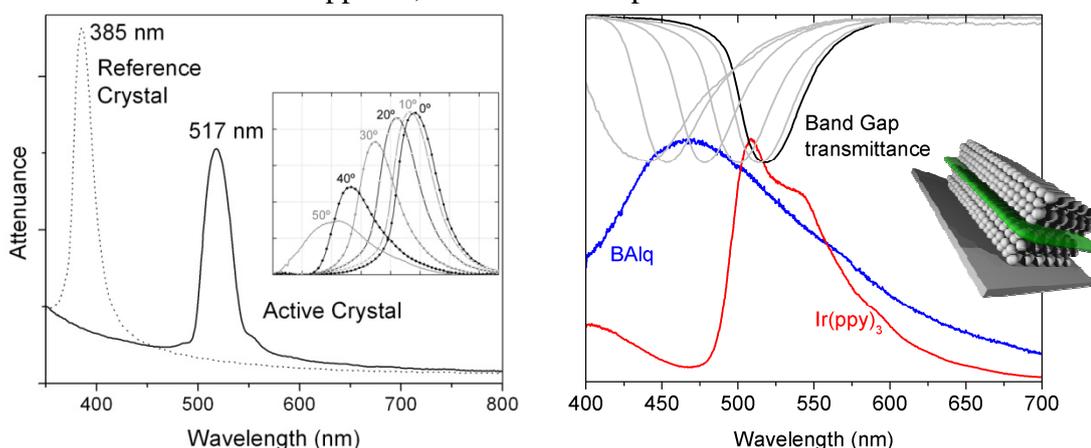


Figure 2. Left; Attenuance spectra from the active and the reference CPhCs. In the inset the angular dependence of the PhBG. Right; Emission from BA1q (blue) and from Ir(ppy)₃ (red) in the PVK film. The optical transmittance of the active CPhC at different angles is plotted on top. In the inset, representation of the sample stack.

Results

In the presence of Ir(ppy)₃ no emission peak from BA1q, at 470 nm, is seen, indicating that energy from BA1q is transferred to Ir(ppy)₃ through FRET.

In the reference PhC (Figure 3-left), where the band gap has no influence on the emission, there is no significant variation on the shape of the emission (figures are normalized at 575 nm) with the concentration of BA1q. In the active PhC (Figure 3-right), however, the intensity from the peak around 500 nm varies strongly with the concentration of BA1q. This result suggests that the high energy substates would be populated not only from the absorption but also through FRET from BA1q molecules.

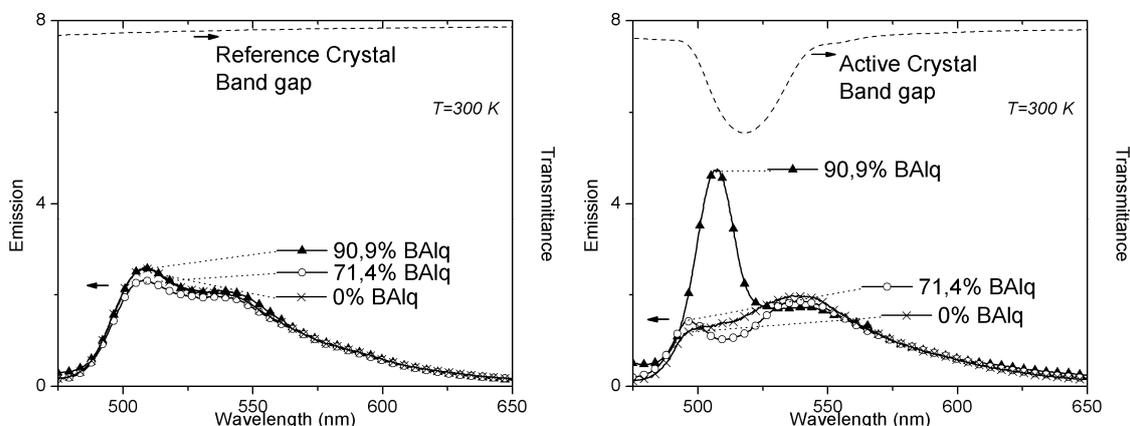


Figure 3. Normalized emission from Ir(ppy)₃ in the reference (left) and in the active (right) CPhC, for different concentrations of BA1q in the polymer film at 300K.

The results at 80 K offer a similar picture, but the enhancement effect is slightly higher than that at room temperature (Figure 4). The fact that the emission is greater at lower temperature clearly indicates that the enhancement is not due to thermal population of the triplet state. At lower temperature the stabilization of the vibrational states leads to a better resonant energy transfer, but in any case the enhancement is mainly driven by the photonic band gap effect.

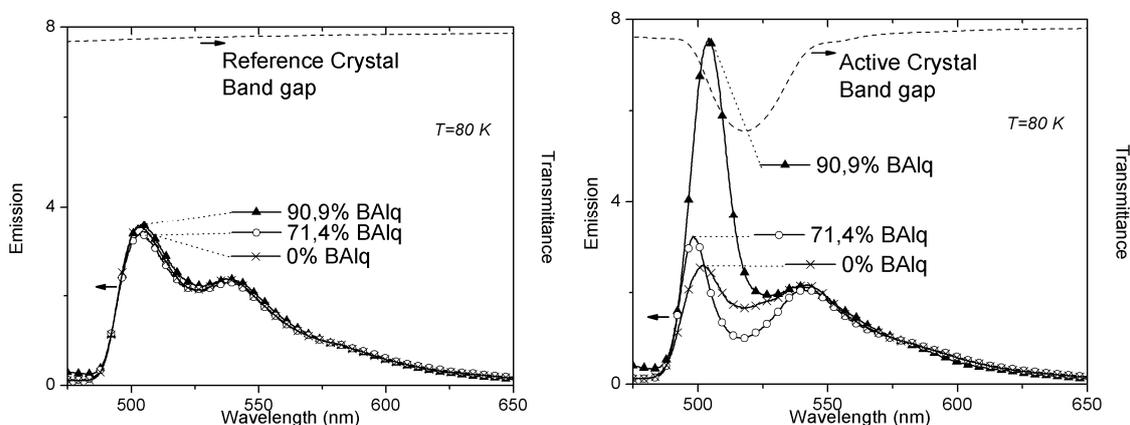


Figure 4. Normalized emission from Ir(ppy)₃ in the reference (left) and in the active (right) CPhC, for different concentrations of BAQ in the polymer film at 80K.

Conclusions

We show how the intensity from Ir(ppy)₃ can be enhanced in the presence of BAQ when inserted in a periodic structure. The suppression of the radiative emission from the BAQ due to optical confinement in a 3-dimensional CPhC helps to populate the excited states of the Ir(ppy)₃ which leads to a high increase of the phosphorescent emission from this molecule. This result proves the enhancement of FRET and shows a large intersystem crossing to the triplet state. The larger decay time of the triplet allows the exciton to diffuse longer distances and therefore, the engineering of thicker active layers should lead to higher efficiencies. Since these organometallic compounds are extensively used in current technologies, the effect can have a highly beneficial impact on many organic systems used in OLEDs and solar cells.

References

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