

Organic Materials for Photonics: Properties and Applications

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I, Giuseppe Carnicella, confirm that the work presented in this report is my own. Where information has been derived from other sources and work which has formed part of jointly-authored publications has been used I confirm that this has been indicated in the thesis.

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To my parents, Titti and Mauro To my brothers, Michelangelo and Marco

Per aspera ad astra

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Pippo

Abstract

Photonics will play a key-role for the future development of ICT and healthcare and organic semiconductors are promising candidates to fulfil the capacity of photonics and deliver on its promises. This "photonics revolution" relies on novel and more performing materials, tailored for the specific requirements of real-world applications, and on reliable and cheap technologies, which can attract investments to address the transition from academia to industry. In this dissertation, I will report my findings on conjugated polymers suitable for photonic applications and demonstrate their use into low-cost photonic structures, as proof of concept.

The first part is dedicated to the study of an aggregation-induced emission polymer, whose fluorescence is enhanced in the aggregated solid-state thanks to the restrictions of intramolecular rotations in contrast to typical planar conjugated polymers. I will show its exceptional fundamental photophysical properties which enable the reduction of non-radiative pathways and makes it attractive for its use in organic light-emitting diodes.

In the second part, I will present the application of conjugated polymers into flexible allpolymer microcavities fabricated through a low-cost process based on spin coating. The incorporation of functional defects in periodic dielectric structures with optical feedback will enable the change in the photonic density of states. I will report the investigation on photonic resonators embedding an aggregation-induced polymer emitting in the visible and a novel nearinfrared oligomer, assessing high quality factors and tuning of their radiative rates to achieve lowthreshold optically pumped lasers.

In the last part, I will show the infiltration of conjugated engineered materials into porous silicon microcavities to enable a novel class of photonically-enhanced chips for communications and sensing. A cheap electrochemical technique has been employed to fabricate one-dimensional resonators, which I characterized fully to demonstrate the variation of the photonic density of states and an efficient approach to novel hybrid photonic devices.

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Table 12: Lifetime values, τ_1 and τ_2 , with relative contribution to PL of each species in brackets of PAH-RhoB and PVA/RhoB in the reference structure and in the microcavity derived by the fit of PL decays in Figure 6.8.

List of publications

- Alessandro Minotto, Petri Murto, Zewdneh Genene, Andrea Zampetti, <u>Giuseppe Carnicella</u>, Wendimagegn Mammo, Mats R Andersson, Ergang Wang, Franco Cacialli, *Efficient Near-Infrared Electroluminescence at 840 nm with "Metal-Free" Small-Molecule: Polymer Blends*, Advanced Materials 2018. **30**(34): p. 1706584.
- Lili Hou, Xiaoyan Zhang, Giovanni F Cotella, <u>Giuseppe Carnicella</u>, Martin Herder, Bernd M Schmidt, Michael Pätzel, Stefan Hecht, Franco Cacialli, Paolo Samorì, *Optically switchable organic light-emitting transistors*, Nature nanotechnology 2019. 14(4): p. 347.
- 3. Alessandro Minotto, Ibrahim Bulut, Alexandros G. Rapidis, <u>Giuseppe Carnicella</u>, Maddalena Patrini, Eugenio Lunedei, Harry L. Anderson and Franco Cacialli, *Porphyrin oligomers beat the energy-gap law in near-infrared fluorescent light-emitting diodes*, submitted to Nature Photonics.
- 4. <u>Giuseppe Carnicella</u>, Alessandro Minotto, Giovanni F. Cotella, Alexandros G. Rapidis, Giuseppe M. Paternò, Egle Molotokaite, Cosimo D'Andrea, Rusli Daik, Guglielmo Lanzani, James W. Feast and Franco Cacialli, *Aggregation-induced emission properties of poly(4-4'-diphenylene diphenylvinylene) with increased solid-state photoluminescence efficiency for organic light-emitting diodes*, in preparation.
- Giovanni F. Cotella, Alessandro Minotto, <u>Giuseppe Carnicella</u>, Qianli Chen, Giuseppe M. Paternò, Francesco Scotognella, Klaus Müllen, Akimitsu Narita, Franco Cacialli, *Efficient Red-NIR light-Emitting Diode Based on Atomically Defined Nanographene Quantum Dots*, in preparation.
- <u>Giuseppe Carnicella</u>, Paola Lova, Giovanni Manfredi, Giuseppe M. Paternò, Giovanni F. Cotella, Ibrahim Bulut, Maddalena Patrini, Cosimo D'Andrea, Francesco Scotognella, Harry L. Anderson, Davide Comoretto, Franco Cacialli, *Near-Infrared Emitters-doped All-Polymer Microcavities*, in preparation.
- 7. <u>Giuseppe Carnicella</u>, Peter Aruffo, Giovanni F. Cotella, Rusli Daik, James W. Feast and Franco Cacialli, *Solution-processed 1D photonic crystals doped with PDPV*, in preparation.
- Valentina Robbiano, <u>Giuseppe Carnicella</u>, Giuseppe M. Paternò, Aline Debrassi Smaczniak, Alessandro Minotto, Stefanie Neutzner, Franco Cacialli, Giuseppe Barillaro, *Engineering the Emission of Rhodamine B by High Quality Porous Silicon Microcavities*, in preparation.
- Michael Hennessey, Dimitri Lezcano, Shabbir M. Mian, <u>Giuseppe Carnicella</u>, Tecla Arcidiacono, Valentina Robbiano, Franco Cacialli, *Polarization Studies of a 3D Photonic Crystal using Transmission and Reflection Experiments*, submitted to American Association of Physics Teachers.

- Alexandros G. Rapidis, Alessandro Minotto, Ibrahim Bulut, <u>Giuseppe Carnicella</u>, Rose Scowen, Harry L. Anderson, Franco Cacialli, in preparation.
- 11. Giovanni F. Cotella, Aurelio Bonasera, <u>Giuseppe Carnicella</u>, Stefan Hecht, Franco Cacialli, *Diarylethenes as optically switchable charge carriers traps in organic light-emitting diodes*, in preparation.
- 12. Giovanni Ligorio, Giovanni F. Cotella, Aurelio Bonasera, Nicolas Zorn Morales, <u>Giuseppe</u> <u>Carnicella</u>, Björn Kobin, Qiankun Wang, Norbert Koch, Stefan Hecht, Emil J. W. List-Kratochvil, Franco Cacialli, *Modulating the luminance of organic light-emitting diodes via optical stimulation of a photochromic molecular monolayer at transparent oxide electrode*, submitted to Materials Horizons.

Impact Statement

Since the first demonstration of a working laser more than half a century ago,^[1] the interest towards photons as information carriers has greatly increased. In the last decade, the huge bandwidth demand in information and communication technology (ICT) and healthcare applications boosted a crucial role of photonics with respect to electronics.

Certainly, within photonics, performances achieved by standard inorganic semiconductors are much more advanced than current characteristics of organic materials. Multiple factors, such as strengthened expertise in design and fabrication of optical devices, topquality facilities and market investments determine a robust supremacy of inorganic semiconductors for high-frequency optical communications. However, to cover fully the capabilities of photonics, a substantial effort is necessary for the synthesis of novel materials which can fit the specifications of niche photonic applications. Organic semiconductors are suitable for applications requiring low-cost fabrication, large active areas and mechanical flexibility. In this scenario, organic materials chemistry has played a significant key role in a prolific research field over the last forty years. In fact, conjugated polymers exhibit physical and chemical properties which can be tailored as needed for specific applications adding a further advantage to the ease of fabrication and mechanical stability.

A large number of conjugated polymers have been employed in an extensive range of applications, from organic light-emitting diodes, (OLEDs)^[2, 3], to organic photovoltaic diodes, (OPVDs)^[4, 5], organic field-effect transistors, (OFETs)^[6, 7] and organic light-emitting transistors (OLETs)^[8, 9]. In addition, photonic devices, including lasers^[10], amplifiers^[11] and modulators^[12], have attracted a strong interest due to the engineering of the optical properties of the active medium, such as absorption and emission wavelengths, photoluminescence quantum yields, oscillator strengths and Stokes' shift. High optical cross-sections, large and ultrafast nonlinear responses and broad spectral tunability constitute important properties of conjugated polymers to photonic applications.

Such exciting properties exploited singularly or properly combined in more complex materials designs feed an almost limitless variety of technological applications relevant to light management, photovoltaics, sensing and lasing. Therefore, two different perspectives need to be investigated to have a full understanding of how research can progress further in this field. In terms of fundamental properties, conjugated polymers still offer interesting scientific challenges which are of interest for both organic chemists and condensed matter physicists. In this regards scientists can take advantage of the control of interchain interactions, i.e. the control of electronic interactions within conjugated chains or between conjugated chains, to modify the chemical, biological and physical properties of a lot of systems^[13], such as for cellular organization^[14] and photophysics of organic semiconductors^[15].

Nevertheless, the control of interchain interactions can improve the performance of photonic and optoelectronic devices based on conjugated polymers properly designed, such as for the restrictions of intramolecular rotations in aggregation-induced emission polymers which boosts photoluminescence^[16] or by engineering the design of side chains of linear oligomers which prevents aggregation^[17]. These innovative material designs provide new classes of materials which can be successfully integrated into simple and low-cost processes for mass scale production. In terms of polymer-based devices engineering, polymer and hybrid planar one-dimensional photonic crystals can respond to the need of costs reduction and fabrication scaling-up for photonic light sources^[18] avoiding traditional expensive fabrication techniques such as lithography and vacuum-based.

Thesis overview

In this dissertation I will show the optoelectronic properties of newly synthesised conjugated polymers and their integration in low-cost devices production for light management and lasing. This dissertation is divided into 7 different chapters.

In Chapter 1 I will introduce the electronic and optical properties of conjugated polymers, describe different approaches to polymers design and their main applications relevant to my research.

In Chapter 2 I will show the aggregation-induced emission properties of poly(4,4'- diphenylene diphenylvynilene) or briefly PDPV, essentially a phenylated derivative of poly(p-phenylene vinylene), PPV, demonstrating how its photoluminescence is boosted in solution when restriction of intramolecular rotations is induced into solvent/non-solvent mixtures.

In Chapter 3 I will describe the implementation of "enhanced" PDPV into organic-light emitting diodes, while in Chapter 4 I will report on all-polymer microcavities embedding PDPV by showing their optical properties and applications to photonics.

In Chapter 5 I will show the electrical and optical properties of a full class of porphyrinbased oligomers and their application into all-polymer one-dimensional microcavities for light management into the near-infrared spectral range (700-1000 nm).

In Chapter 6 I will present the optical characterisation of hybrid one-dimensional photonic crystals based on porous silicon and doped with Rhodamine B derivatives.

In Chapter 7 I will summarize other works I have not reported in this thesis, but I have contributed to regarding 3D photonic crystals, near-infrared light-emitting diodes and organic light-emitting transistors.

1 Conjugated polymers: properties and applications to photonics

1.1 Electronic properties

Conjugated materials are organic semiconductors whose electronic properties derive from the orbitals of the carbon atom: $1s^2 2s^2 2p^2$, from which two electrons in the *p* orbital can form bonds with other atoms.^[19] However, carbon atoms have four valence electrons and, considering the sp^N hybridisation between atomic orbitals, can hybridise in three possible configurations, sp^3 , sp^2 and sp^1 , with N+1 sp^N hybridised orbitals and 3-N non-hybridised *p* orbitals, as shown in Figure 1.1 (orbitals size has been drawn constant for simplicity).

The molecular orbitals σ and π result from bonding two neighbouring carbon atoms for each sp^N hybridisation. A σ bond is a bond between two sp^N orbitals of two carbon atoms (each one offering one electron), while a π bond is a bond between two p orbitals of two carbon atoms (each one offering one electron).



Figure 1.1: (a) sp^3 hybridization – tetrahedral structure with an angle of 109.5° between the four sp^3 bonding orbitals, which can form four σ molecular orbitals. (b) sp^2 hybridization – trigonal-planar structure with three sp^2 orbitals spaced by an angle of 120° in the same plane and a *p* orbital standing perpendicularly. (c) sp^1 hybridization – planar geometry with two sp^1 orbitals with an angle of 180° and two *p* orbital standing perpendicularly each other and with respect to the sp^1 hybridized one.

Saturated polymers, such as alkane-based polymers, are sp^3 hybridised, have each carbon atom forming four σ orbitals when bonded to a neighbouring carbon atom and exhibit an insulating behaviour as the energy required to promote an electron to the conduction band is higher than 8 eV. Differently, conjugated materials rely on carbon atoms sp^2 hybridised, which results in the formation of three coplanar bonds (σ bonds), each 120°-far away from the others, with adjacent atoms. The remaining *p* orbital is not hybridised, stands perpendicularly to the σ bonds and is overlapped with an available neighbouring carbon atom *p* orbital, forming a π orbital which is a double bond. In a linear chain, this overlap creates an alternation of single and double bonds which is characteristic of conjugated polymers, based on unsaturated compounds such as ethylene.

The π orbital has two split energy levels, namely π -bond and π^* -anti-bond, as shown in Figure 1.2,^[20] where the ethylene molecule C₂H₄ is used as example. When the number of carbon atoms is high as for real polymers such as for polyacetylene reported in Figure 1.2, π and π^* energy level of carbon atoms degenerate in two quasi-continuous energy bands where bonding π - orbital is the highest occupied molecular orbital (HOMO), while the anti-bonding π^* -orbital is the lowest unoccupied molecular orbital (LUMO). The energy splitting is larger if the overlap of p orbitals is more significant and represents the energy necessary to promote an electron from a ground to an excited state (~1-3 eV in conjugated polymers).^[21] A quantitative prediction of energy splitting can be derived by using the Linear Combination of Atomic Orbitals, LCAO.

Although in the solid state polymeric chains interact through secondary forces such as Van der Waals which complicate the use of LCAO model, the electronic properties of conjugated polymers can be approximated taking into account the HOMO-LUMO position and their energy difference defined as Energy Gap.^[22]

In the past, theoretical studies hypothesised that conjugated polymers had a metallic behaviour, hence the Energy Gap almost closed, due to a constant distance between carbon atoms, which would induce a complete delocalisation of the electron wavefunction on the entire polymer and a minimisation of the molecular energy. However, the actual distortion for the displacement of alternating nuclei in the chain is due to the Peierls distortion,^[23] known well before the discovery of the electrical conductivity of doped polyacetylene in 1977. Peierls studied the distortion of a periodic lattice of a one-dimensional crystal due the atomic oscillations, which break its order. Similarly, considering a polymeric chain as a one-dimensional crystal, the displacement of carbon nuclei lowers the symmetry of the system and results in short (double) and long (single) bonds, therefore a band separation is localised at the edge of the Brillouin zone, which implies the semiconducting behaviour of conjugated polymers.^[24] Therefore, in Figure 1.2, the two quasi-continuous bands of polyacetylene, namely HOMO and LUMO, are separated by a non-null and low Energy Gap ($E_g = 1.5 \text{ eV}$ for polyacetylene), typical of semiconductors.



Figure 1.2: Scheme of the energy splitting of 2 *p* orbitals into 2 different molecular orbitals, π and π^* . On the right, the increase of the conjugation length leads to formation of quasi-continuous bands.^[20]

1.2 Optical properties

Conjugated polymers possess appealing optical properties, such absorption and emission wavelengths which can be tuned from the visible (400 nm $< \lambda_{vis} < 700$ nm) to the near-infrared (700 nm $< \lambda_{NIR} < 1000$ nm) range of the spectrum, high photoluminescence quantum yields (close to unity), strong oscillator strengths and tuneable Stokes' shift. The optical features of these polymers are described by the Jablonski diagram^[25] shown in Figure 1.3, which illustrates schematically the lowest-energy electronic transitions. The ground state, S_0 , is a singlet state (i.e. total spin quantum number S = 0), and S_1 and S_2 are singlet excited states. The triplet excited state (i.e. total spin quantum number S = 1) is T_I . Each electronic state is split in several vibrational states, whose typical energy separation is typically a fraction of meV.

The vertical transition from the ground state to the singlet excited states is named absorption, which occurs on a fs timescale. Electrons promoted to S_2 relax to the energy-lowest S_1 by internal conversion and emitting no energy (no radiative processes) on ps timescale. From S_l level the molecule can return to the ground electron state (Kasha's rule) by a process occurring in a ns timescale (fluorescence). After an electron is promoted to an excited state Pauli's exclusion principle does not impose any restriction on the spin. However, in the fluorescence process, the transition is "spin-allowed", i.e. the electron in the excited state has opposite spin to the second electron in the ground state, and the generated singlet has a short lifetime (from tens of ps to tens of ns), which depends on the inverse proportionality with the sum of radiative (k_R) and non-radiative (k_{NR}) rates of the molecule. Instead, the phosphorescence process, which consists of a radiative transition from T_{I} to the singlet ground state, is not spin-allowed (both electrons have the same spin orientation), but takes place due to a spin conversion process known as intersystem crossing (ISC) occurring over longer timescales (μs to > ms). The intersystem crossing constitutes a way to populate the T_I state and can be favoured by inserting heavy atoms like palladium and platinum in the synthesis of conjugated polymers. These heavy metals increase the yield of ISC through a larger spin-orbit coupling but is detrimental for the biocompatibility of such polymers.^[26]

The Frank-Condon principle^[19] states that nuclear motion is much slower in time than electronic transitions, that are therefore virtually "instantaneous" and thus favoured between vibrational levels corresponding to minimal change in the nuclear coordinates. Indeed, an electronic transition is more likely to take place when the wavefunctions of the initial and final are strongly overlapped. The principle is applicable to both absorption and emission transitions. Furthermore, the emission spectrum is red-shifted with respect to the absorption spectrum and the absorption and emission spectra exhibit maxima whose energy difference is called Stokes' shift.



Figure 1.3: Jablonski diagram^[27] illustrating different electronic and vibrational levels in an organic molecule, and possible optical transitions for the lowest energy states.

In real polymers the fluorescence properties, i.e. the light emission following the absorption of photons, can be changed also by the surrounding environment. As such the fluorescence intensity can be decreased due to several factors, such as impurities and/or defects, e.g. catalyst residues or other contaminants deriving from the synthesis or contact with quenchers. This phenomenon is known as quenching and is detrimental to the photoluminescence yield of conjugated polymer-based devices, where the photoluminescence quantum yield is defined as the number of photons emitted as a fraction of the number of photons absorbed. Quenching is always present in solutions or liquid phases, but the effect of quenchers in solid-state is higher. Indeed, molecular aggregation also called concentration quenching caused by intermolecular van der Waals forces is the most important cause of quenching in solid state and can change the optical properties of conjugated polymers. Two types of aggregates can be identified, shown in Figure $1.4^{[28]}$: a) *H*-aggregates (co-facial aggregation of monomers) and b) *J*-aggregates (head-to-tail aggregation of monomers).



Figure 1.4: Arrangements of *H*- and *J*-aggregates for a dimer and conjugated monomer with effects in the absorption spectra: blue-shift for *H*-aggregate and red-shift for *J*-aggregate with respect to the monomer absorption spectrum.^[28]

In *H*-aggregates there is a stack of two or more monomers perpendicularly to the molecular plane, while in *J*-aggregates the monomers are parallel to the molecular plane. In particular, in *H*-aggregates high-energy transition is favoured, photoluminescence quantum yield is decreased for the unfavourable level splitting and absorption spectra are blue-shifted. Instead, *J*-aggregates result in a red-shift of the optical absorption and emission and high quantum yield and are much more interesting for optoelectronic and photonic applications. The red-shift of the optical absorption and emission of *J*-aggregates has been attributed to the large excitonic coupling along the *J*-aggregate axis, which arises entirely from the Coulombic intrachain interactions.^[29]

1.3 Materials for photonics and optoelectronics

The technology demand for highly luminescent materials has driven researchers to the study and development of uniquely synthesised compounds, designed to cater for lighting, displays and biomedical devices.^[30-36] In particular, organic conjugated chromophores are attractive for a broad range of applications, such as light-emitting diodes, plastic lasers and

sensors, all requiring high fluorescence in the solid state.^[10, 37-46] Many conjugated materials are highly emissive in dilute solutions and exhibit fluorescence quantum yields close to unity. Nevertheless, in the solid state, organic dyes tend to form poorly emissive aggregates called *H*- aggregates, whose formation is driven by the π - π interaction between the conjugated moieties incorporated in the backbone of the chromophore. To limit such aggregation-caused quenching (ACQ) mechanism and increase the solid-state photoluminescence efficiency, different strategies have been developed, such as dilution of chromophores in solid-state matrices^[17, 47-49] or molecular design^[50-52] which proved to be effective and favoured the widespread integration of conjugated emitters in many light-emitting devices, nowadays available in the market.

A relatively recent approach to tackle ACQ is the design of aggregation-induced emission (AIE) molecules, in which non-emissive chromophores are induced to emit by the formation of aggregates.^[53] While in the ACQ the π - π stacking interaction due to typical disk-like shape of organic molecules promotes the decay of the exciton through non-radiative channels, the rotating phenyl rings of a propeller-shaped structure undergo the restriction of the intramolecular rotations (rotations and vibrations) in the aggregated solid state which decreases the non-radiative constant, thus boosts the photoluminescence. An archetype of AIE chromophores is tetraphenylethylene (TPE), in which four peripheral phenyl rings surround the central olefin stator. As a result of the TPE chemical structure, in dilute solutions, the characteristic propeller-shaped peripheral phenyl groups are free to rotate enabling non-radiative relaxation channels and quenching the fluorescence. By contrast, in the aggregated solid state, physical constraints restrict the rotation of phenyl groups, enabling the radiative decay of the exciton, thus brightening the emission.^[54, 55] Figure 1.5^[16] shows an exemplifying perylene planar molecules which tend to aggregate as discs pile up against non-planar hexaphenylsilole (HPS) molecules whose phenyl rotors experience restricted intramolecular rotation against the silole stator in the aggregate states increasing their emission.

In 2001, the first report^[53] on the AIE phenomenon raised a great interest for the development of innovative macromolecular designs where aggregation plays a constructive role for luminescence. This field and the related number of publications have grown impressively

since 2007, when the AIE behaviour was completely characterised by Ben Zhong Tang and coworkers.^[53, 56, 57] The possibility of turning-on the luminescence in the solid state is extremely exciting for real-world devices expanding the spectrum of applications to biological sensors, chemical probes and optoelectronic and photonic devices.^[58] In this thesis I will report on the characterisation of a phenylated derivative of PPV and its applications to photonics and optoelectronics.



Figure 1.5: (A) Planar perylene structures favours strong π - π stacking interactions, i.e. *H*-aggregates which quench photoluminescence. (B) Non planar hexaphenylsilole (HPS) propeller-shaped structure boosts photoluminescence intensity.^[16]

Another emerging class of semiconductors for photonic applications is constituted by supramolecular conjugated polymers. Polymerization had a dominant role in chemistry throughout the last century, but supramolecular chemistry has revolutionized the field in the last two decades. In 1987 Jean Marie Lehn's work (with Charles J. Pedersen and Donald J. Cram) was recognized with the Nobel Prize having introduced the concept of supramolecular chemistry as the chemistry of the intermolecular bonds.^[59] While molecular chemistry is ruled by covalent bonds, supramolecular chemistry is the area of chemistry of noncovalent interactions among subunits or components. Weak forces, such as intermolecular forces, electrostatic or hydrogen bonding, are investigated and manipulated to give rise to new entities of higher complexity which have unique properties different from the starting molecules.

In particular, supramolecular materials examine noncovalent linkages, such as hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π - π interactions and electrostatic effects, to connect building blocks of any size.^[60] Electronic and optical characteristics of supramolecularly-engineered conjugated materials are affected by the chemical composition, the primary molecular architecture (how monomers are linked in the polymer chain by covalent bonds) and the supramolecular interactions (secondary and tertiary forces, typical of proteins^[61]). The latter allow to manipulate the interplay between molecules and chains leading to the synthesis of novel organic engineered materials suitable for optoelectronics and photonics.

The molecular design stimulated the emergence of a large class of novel organic materials which can be classified by their molecular organization, either in coiled chains^[62] or ordered filaments^[63]. The former generate random coiled chains without internal order analogously to common polymers, the latter create highly ordered structures leading to one-dimensional wires. The control of intermolecular interactions creates liquid crystalline materials, monolayers or complex self-assembled architectures, whose exploitation is useful for a plethora of applications ranging from organic electronics to nano-engineered photonic devices. For instance, high charge mobilities have been obtained by self-assembly of conjugated polymers into supramolecular nanofibers useful for organic field-effect transistors and solar cells,^[64] whereas reduced quantum yield due to the formation of intermolecular excited states in luminescent materials can be avoided by investigating intermolecular π - π interactions.^[52] Two significant examples of supramolecular materials are rotaxanes and perylene bisimide compounds.

Conjugated rotaxanes (Figure 1.6) represent a remarkable case of a class of semiconducting organic materials engineered at a supramolecular level.^[52] They consist of a luminescent conjugated backbone, such as *poly-(para-phenylene)* or polyfluorene, threaded through α - or β - cyclodextrin rings (sketched as green-shaded cones in Figure 1.6), stopped at both ends of the chain to avoid unthreading. The solid-state packing effect that causes partial quench of the photoluminescence is prevented by the cyclodextrin rings and enables ultra-broad gain bands in blends of rotaxanes with emissive conjugated polymers,^[65] useful for optical amplifiers and lasers. This approach is favourable to preserve the optical properties of uninsulated

conjugated backbones but takes advantage of cyclodextrins volume to keep a fixed minimum separation between π -bounds.



Figure 1.6: *Poly(para-phenylene)*-based rotaxane structure retieved from Ref. [65]. The luminescent conjugated backbone, such as *poly-(para-phenylene)* or polyfluorene, is threaded through α - or β - cyclodextrin rings (green-shaded cones), stopped at both ends of the chain to avoid unthreading.

Another significant example of supramolecular design is offered by perylene bisimides (PBIs) compounds, used as pigments for automotive coatings and laser dyes, whose quantum yields have been reported in literature to be ~100% in solution.^[66] By engineering *H*-bonds, highly fluorescent *J*-aggregates,^[67] shown in Figure 1.7, have been synthesised increasing the fluorescence of PBIs in the solid state, essential for photonic applications. In *J*-aggregates, the monomers are head-to-tail bound, parallel to the molecular plane, and constitute a nanowire, hence they have strong electron delocalization. Furthermore, *J*-aggregates have absorption bands shifted towards longer wavelengths than the correspondent monomer, a nearly resonant fluorescence (very small Stokes' shift) and extended domains of coherent transition dipoles enabling higher fluorescence efficiency relying on the beneficial effect of hydrogen bonds which hinder the formation of *H*-aggregates which favour the quenching of the luminescence due to the reduced transition dipole moment.

A further example of molecular design is the synthesis of conjugated polymers/oligomers with unique features to tackle aggregation quenching which is a huge limitation when dealing with luminescent materials and their relevant applications. In fact, the most common planar structure of emissive polymers which turns the photoluminescence off due to the formation of *H*aggregates can be improved by the addition of side-chains which prevent π - π stacking thanks to their steric hindrance. This interesting feature will be analysed in this thesis where I will show the optical and electrical characterisation of a class porphyrin oligomers emitting in the near infrared range of the electromagnetic spectrum.

Conjugated polymers have been widely characterised and integrated into photonics structures.^[68, 69] Nevertheless, the countless possibilities of polymers synthesis given by organic chemistry stimulate the development of new strategies for the insertion of luminescent materials into photonic structures. In this thesis I will discuss the optical characterisation of Rhodamine B derivatives designed to avoid aggregation quench and loaded into porous silicon microcavities.



Figure 1.7: Schematic illustration of the *J*-aggregates of PBIs retrieved from Ref. [67]. The top perylene bisimide dye monomer is the building block of the extended hydrogen-bonded *J*-aggregate shown at the bottom. Red and orange twisted blocks represent the perylene bisimide cores in the chain, grey cones with a blue apex represent the substituents in the monomer, and green lines represent hydrogen bonds. The dyes self-assemble in a helical fashion.

1.4 Photonic and optoelectronic conjugated polymers-based devices

Conjugated polymers are of great interest for their incorporation within photonic and optoelectronic devices, such as lasers, amplifiers, light-emitting diodes, waveguides and modulators. Although the semiconductor industry has being able to satisfy the Moore's law, the up-scaling of the working frequency has been determining the gradual replacement of electrical interconnections with optical components. Integration technologies and down-scaling of devices are key-factors for this fascinating challenge, but organic semiconductors-based devices offer a supplementary advantage due to their flexibility and tunability which apply well for applications such as visible light communication systems (VLCs)^[70], smart organic luminaires^[71] and cheap (bio)lab-on-chips (LOC)^[72].

Optically-pumped organic semiconductor lasers (OSLs) have been reported in a broad variety of configurations, including Distributed Bragg Reflector (DBR)^[73] and Distributed Feedback (DFB)^[74] lasers. They are easy to integrate into waveguides or optical fibres^[75], by means of soft lithographic techniques, and highly tuneable over the whole visible spectrum^[76] until 1 µm. On the other hand, plastic photonic crystals became technologically relevant for the ease of fabrication i.e. processed from solution and a range of application from light management to sensing in any spectral range which attracted considerable interest.^[18, 77] Nevertheless, allorganic electrically-driven OSLs have not been demonstrated yet although a first indication of current-injection lasing has been reported in 2019.^[78] Electrically-driven OSLs constitute the major challenge for the field especially for the intrinsic limit of organic electrical devices to operate fast enough to produce nanosecond pulses. As such, loss mechanisms, such as charge generation and quench of the photoluminescence, should be reduced as much as possible and the control of molecular interactions is a fascinating route to be run by means of molecular design, e.g. rotaxanes^[79] or dendrimers^[80] which also allow to have low loss waveguides. The use of the same active material in both OSLs and passive waveguides has the potential to tackle a recurring request for cheap plastic lab-on-chip for bio-medical or microfluidic applications^[72], as shown in Figure 1.8.



Figure 1.8: Scheme of an exemplary LOC integrating DFB lasers (500 μ m length and 300 μ m wide), passive waveguides (4.5 mm length and 300 μ m width) and a microfluidic channel (7.5 mm length and 0.1 mm width), retrieved from Ref. [72].

Optical amplifiers represent another basic building-block for photonics, especially in optical networks to transmit data. Although inorganic amplifiers fit very well requirements of long-distance communications, organic amplifiers are inexpensive as they are solution processable and their integration is feasible with a large number of materials. Conjugated polymers absorb strongly and exhibit notable gain coefficients, which makes them excellent candidates for compact integrated circuits. For example, Amarasinghe *et al.* reported an amplifier with an amplification factor, A = 32 dB, where a well-known co-polymer, i.e. poly(9,9)-dioctylfluorene-co-benzothiadazole (F8BT), is used as active material embedded within a slab waveguide and between two gratings, advantageous for the light coupling.^[81]

Despite the high gain already demonstrated for organic semiconductors and similar to erbium-doped silica fibre amplifiers, efforts in their synthesis to extend their gain lifetime (typically <300 ps) are still essential to have strong population inversion asynchronous with the pump for stimulated emission.^[82] Similar issues involve also the operation of OSLs for which continuous wave (*CW*) pumping would be the best solution, however non-radiative emission constitutes the main contribution to loss and preclude their correct operation. Once again, molecular design of active materials helps decreasing the loss of the ground state and optical amplification from rotaxanes as demonstrated for instance by Brovelli.^[65]

Photonic integrated circuits (PICs) need also efficient modulators for logic operations. The electro-optic modulator represents the most adopted configuration. The intensity of the light, coupled and guided through the structure, is changed by applying an external electric field which modifies the optical properties of the electro-active material. In particular, the variation of the squared refractive index of this material is inversely proportional to the applied electric field by electro-optic coefficients, r_{ijk} , $(\Delta(1/n^2)_{ij} = r_{ijk}E_k$ where *i*, *j*, *k* are orthogonal versors), typical of each material (electro-optic tensor). The best known and most valuable electro-optic material is lithium niobate, whose coefficients have been surpassed by electro-optic polymers by a factor of six.^[83] Alternatively, non-linear processes, inducing changes in the refractive index of the active material embedded in a photonic crystal with ultrafast response (~10 ps) or gain switching in conjugated polymers by confinement of the excitation through polymer chain isolation, are two mechanisms investigated in Ref. [84]-[85]. A third approach is the hybrid integration of nonlinear organic materials within inorganic structures which guarantee robust designs. Four-wave mixing technique was used to demonstrate optical switching under 500 ps.^[85]

Passive components are essential to carry data in optical networks. Low-loss polymeric waveguides compete with inorganic materials even if the confinement is lower due to the lower refractive index contrast. Temperature-independent operation, easy integration with other components and technology platforms and inexpensive 3D fabrication constitute the main advantages of the use of polymers. In addition, several techniques such as direct writing^[86], self-organization^[87] and soft-lithography^[88] have been investigated for their realization. Among others, direct writing can use nonlinear processes to fabricate higher refractive index regions by focusing the laser and polymerizing the photosensitive material obtaining transmission losses of the order of 0.1 dB mm⁻¹.^[89]

In the flourishing field of organic photonics I will provide an overview on properties and applications of 1D photonic crystals I have been dealing during my research.
1.4.1 1D Photonic Crystals

Three decades ago John^[90] and Yablonovitch^[91] were pioneers in the field of photonic crystals (PhCs) whose technological importance has been growing with no interruptions. PhCs are structures in which materials with different dielectric properties alternate periodically in one, two or three directions affecting the properties of photons which interact with them as per electrons in a crystalline semiconductor.^[92] As such, three concepts of solid-state physics for crystals can be transposed to PhCs i.e. the photonic band structure, which determines spectral regions in which photon propagation is allowed or forbidden; the photonic band gap (PBG), from which the chromatic response of the PhC is determined; the density of photonic states (PDOS), whose changes affect the photoluminescence of an embedded active material.

Distributed Bragg Reflectors (DBRs) are one of the most interesting classes of photonic crystals with a periodicity in a single dimension. DBRs are lattices of thin films made of two transparent media with refractive indices n_1 and n_2 and thicknesses d_1 and d_2 alternating in one direction (periodicity = $d = d_1 + d_2$), e.g. x as shown in Figure 1.9a. When light is incident in the direction of their periodicity the sum of subsequent reflections, refractions and transmissions at the interfaces of each layer generates constructive and destructive interference effects at every wavelengths defining univocally the spectral region of PBG where light cannot propagate, i.e. incident light is entirely reflected as between 630 nm and 750 nm for the example DBR optical response simulated in Figure 1.9b.



Figure 1.9: (a) DBR schematic with constituting two materials alternating along *x*-direction with refractive indices n_1 and n_2 and thicknesses d_1 and d_2 , respectively. (b) Calculated reflectance spectrum of a DBR with 25 bilayers ($d_1 = 105$ nm, $n_1 = 1.67$, $d_2 = 120$ nm, $n_2 = 1.46$).

The peak spectral position of the stop band, λ_{peak} , is described by Eq. (1.1) and varies with the angle of the incident light (dispersion). As the incidence angle increases, λ_{peak} moves towards lower wavelengths for both polarizations of the light. However, while for *S*-polarization the optical features of the PBG remain almost unchanged, for *P*-polarization the reflectivity intensity and the width of the optical response of the DBR decreases approaching the Brewster angle.^[93]

$$\lambda_{\text{peak}} = \frac{4n_1n_2}{n_1 + n_2}d\tag{1.1}$$

Notably, Eq. (1.1) is a simple analytical expression for determining the peak wavelength of the stop band when the $\lambda/4$ condition is satisfied. This condition states that when the optical thickness of each layer is the same, i.e. $n_1d_1 = n_2d_2 = \lambda/4$, the even-numbered higher order appearances of the stop band will be suppressed, allowing the transmission of light to be nearly uninterrupted for a wide spectral range outside of the stop band. Furthermore, the satisfaction of this condition will also result in the widest stop band for a given bilayer thickness. If the DBR fulfils the $\lambda/4$ condition the intensity of reflectance, *R*, of the PBG which is reported in Eq. (1.2) with *N*, the number of bilayers and $n_2 < n_1$, is maximized.

$$R = 1 - 4\left(\frac{n_2}{n_1}\right)^N = 1 - 4\left(1 - \frac{\Delta n}{n_1}\right)^N$$
(1.2)

where Δn is the dielectric contrast between the two media, which determined also the spectral width of the PBG as per Eq. (1.3). The larger is the dielectric contrast in the DBR the wider is the stop-band of the DBR, which is reported in Eq. (1.3), derived by the perturbation theory and valid for weak Δn .^[92]

$$\Delta E_{PBG} = \frac{4E_{PBG}}{\pi} \frac{n_1 - n_2}{n_1 + n_2} = \frac{4E_{PBG}}{\pi} \frac{\Delta n}{2n_2 + \Delta n}$$
(1.3)

In a DBR the light propagation is never inhibited for all directions and for all polarizations being the PBG incomplete.^[92] However, a DBR can homogenously reflect light normal to the direction of periodicity over the spectral band called PBG as shown in Figure 1.9. Nevertheless, if a defect layer breaks the periodicity of the system a planar microcavity is created. The cavity layer with thickness d_c and refractive index n_c as per Figure 1.10a creates allowed photonic states within the PBG, changing the optical response of the structure, where a sharp feature gives a minimum in reflectance within the PBG as shown in Figure 1.10b. The spectral position of this minimum, λ_c , which is also called cavity mode can be easily derived by the resonance condition in the cavity. For the first order resonance, $\lambda_c = 2n_cd_c$ and its full width at half maximum $\Delta \lambda_c$ defines the microcavity quality factor as $Q = \lambda_c / \Delta \lambda_c$. Higher Q-factors result in sharper cavity mode with threshold reduction in microcavity laser devices.^[18]



Figure 1.10: (a) Scheme of a microcavity consisting of two materials alternating along *x*-direction with refractive indices n_1 and n_2 and thicknesses d_1 and d_2 , respectively whose periodicity is broken by the insertion of the cavity layer of refractive index n_c and thickness d_c . (b) Calculated reflectance spectrum of a microcavity composed by two DBRs of 25 bilayers ($d_1 = 105$ nm, $n_1 = 1.67$, $d_2 = 120$ nm, $n_2 = 1.46$) with a cavity layer in between ($d_c = 175$ nm, $n_c = 2$).

The presence of such a minimum in the reflectance spectrum allows the incidence light to be partially transmitted within the structure. Therefore, if the cavity layer is an emitting material the photonic structure can modify the fluorescence of such emitting layer according to the fundamental light-matter processes. Indeed, the Fermi's golden rule adapted to PhCs^[94] says that optical transitions rates, k_R , depend on the photonic density of states (PDOS, ρ) as per the below Eq. (1.4)

$$k_{R}(\omega) \propto \int \rho(\bar{r},\omega) d\bar{r} \tag{1.4}$$

As shown in Figure 1.11a, in a homogeneous medium the PDOS is monotonic. On the other hand, in a DBR it is almost nullified in the spectral range where the PBG insists with a slight increase at the PBG edges as in Figure 1.11b. Therefore, within the PBG the emission rate is proportionally reduced. Eventually, in a microcavity as per Figure 1.11c, the PDOS has a peak occurring at the cavity mode, where per Eq. (1.4) the emission rate is supposed to increase.

In a microcavity, the fluorescent cavity layer shone by the light partially transmitted through one of the constituting mirrors emits photons whose energy distribution can be significantly modified by the variation of PDOS, i.e. fluorescence is zeroed where the PBG of the photonic structure has maxima in its reflectance spectrum while it is increased in the cavity mode where photons are funnelled. The variation of PDOS should affect also the emission radiative rate, i.e. the total radiative rate in a microcavity is enhanced into the cavity mode and reduced in the PBG, and this effect can be quantified by lifetime measurements at single wavelengths and results to be more significant whether the spectrum of the emitting material becomes particularly sharp or a strong spatial confinement is obtained in the microcavity. Either ways the *Q*-factor value becomes crucial, however *Q*-factors are strongly dependent on the quality of the fabricated structure and on the technology adopted. Typical values of quality factor span from a few hundred for all-polymeric or hybrid structures^[95] to millions for integrated resonators^[96]. Being the *Q*-factor strongly affected by the material processability and dielectric constants of used materials is still subject of research in order to boost potential applications of organic and hybrid microcavities, which will be described extensively in following chapters.



Figure 1.11: Schematics of the PDOS in (a) free space, (b) in a DBR, and (c) in an MC, retrieved from [18].

2 Aggregation-induced emission properties of PDPV

2.1 Introduction

Leveraging the aggregation induced emission (AIE) is an effective approach to the molecular design of emissive conjugated polymers. The typical propeller-shaped structure with rotating phenyl rings restricts the intramolecular rotations decreasing the non-radiative rates due to internal rotations and vibration, thus increasing the photoluminescence.

So far, most of the papers regarding AIE have been related to low-molecular weight molecules to be deposited in films by expensive techniques (vacuum sublimation, vapour deposition, etc.). However, low-cost practical applications for large-area devices require depositions by easy and cheap methods such as spin-coating. Hence, many groups have focused their efforts on the polymerisation of well-known AIE molecules, synthesising high molecular weight AIE polymers with good solubility in common organic solvents, having an exceptional capacity of filming.^[97, 98] In light of the broadly accepted AIE mechanism description, the photophysical characterisation of propeller-shaped polymers is useful to gain a better insight on their operation in devices, such as organic light-emitting diodes (OLEDs), and to suggest possible routes to improve their performances. Nevertheless, the already occurring enhancement of the photoluminescence quantum yield in solid state due to the suppression of non-radiative decay channels can be further boosted by using the AIE material blended with organic polymers.^[99] This approach has been profitably used to increase the external quantum efficiency of solution-processed OLEDs as I will report in Chapter 3.

Among several classes of AIE-active polymers,^[97] poly(phenylenevinylene)s (PPVs) cover a role of the uppermost importance, having been widely used and studied for OLEDs since 1990.^[38] In particular, phenylated derivatives of PPV have been already investigated for their outstanding photoluminescence and electroluminescence properties.^[100, 101] The introduction of

cis-vinylene units into PPV was found to improve the photoluminescence efficiency, already in 1995, and explained as due to the higher degree of disorder of these active films.^[102] Indeed, the disorder, restricting the exciton diffusion range, reduces the chance of non-radiative decay. Furthermore, Cornil^[103] calculated that, upon aggregates formation, changes in the orientation of the molecules (e.g. perpendicular to one other) prevent the PL quenching, laying the foundations for the later explanation of AIE phenomenon.

However, incidentally, the chemical structure of some PPV derivatives resembles the propeller shape, typical of tetraphenylethylene (TPE). Recently, linear *poly*-TPEs have been reported in literature showing increasing photoluminescence efficiencies in the solid state compared to solutions, thus AIE behaviour.^[98] Hence, it is worth to offer a new interpretation of previously reported data of PPV derivatives, considering the beneficial effect of the aggregates formation to their photoluminescence efficiency.

Here, I investigate the AIE properties of *poly*(*4-4'-diphenylene diphenylenevinylene*), or briefly PDPV, which is a phenylated derivative of PPV, having the vinylic hydrogen atoms substituted with phenyl rings. The chemical structure of PDPV is reported in Figure 2.2. This modified PPV exhibits an increased photostability, which slows down the photo-oxidative degradation.^[104] Furthermore, the introduction of phenyl rings, which enables good solubility in common organic solvents, was already assessed as advantageous to boost the photoluminescence efficiency in the solid state.^[101] The high photoluminescence efficiency was attributed to the *cis:trans* content.^[105] Namely, the chemical structure of the material inhibits its crystallisation and the disorder leaves sufficient free volume available for the molecule rearrangement in the most favourable configuration. Hence, the highest photoluminescence efficiency has been measured for a 50:50 *cis:trans* content which leads to the most energetically disordered chains arrangement.

Interestingly, according to the quantum chemical calculations on PDPV, the most stable conformation of the isolated PDPV polymer chain presents the lateral phenyl groups perpendicular to the main backbone.^[101] The latter restricts the intramolecular rotations and induces a degree of disorder, leading to an enhancement of the emission, in analogy to the one observed with molecular AIE materials. I will present steady-state and time-resolved

photoluminescence (PL) spectroscopy of PDPV, in dilute solution and solid-state films and the characterization of the steady-state and time-resolved PL spectroscopy of PDPV in solutions containing increasing amount of non-solvent, thus inducing the formation of aggregates.

2.2 Experimental methods

Solutions preparation. The synthesis protocol of PDPV was reported in [106]. PDPV (Mw = 28,100, Mn = 19,280) was dissolved into toluene at the concentration of $5x10^{-2}$ mg/ml (dilute solution) and at the concentration of 10 mg/ml for the solid state film, spun onto a fused silica substrate at 800 rpm. For the titration process, the concentration of PDPV was kept constant at $5x10^{-2}$ mg/ml and the ratio in the mixture between toluene (solvent) and 2-propanol (IPA, non-solvent) changed accordingly, as described in the results section.

Spectroscopic characterization of PDPV. Optical absorption spectra were measured using an Agilent 8453 UV-Vis spectrophotometer. CW were carried out exciting with a ps-pulsed diode laser (pulse duration = 40 ps, λ_{exc} = 375 nm) and detecting the PL with a spectrophotometer (Andor Shamrock 163i) coupled with an Andor Newton CCD unit cooled to -50°C.

Photoluminescence quantum yield measurements. The PL quantum yield or efficiency, η , of chromophores is calculated as the ratio between the number of emitted photons and the number of absorbed photons. The technique used in this work to measure η of both solutions and solid films is the integrating sphere^[107] implemented by exciting with a ps-pulsed diode laser (pulse duration = 40 ps, λ_{exc} = 375 nm) and detecting the PL a spectrophotometer (Andor Shamrock 163i) coupled with an Andor Newton CCD unit cooled to -50°C.

Time correlated single photon counting (TCSPC). The time-correlated single-photon counting is a robust tool to measure the photoluminescence temporal decays of chromophores.^[26]

It is based on the assumption that for low-level and high-repetition signals the light intensity is so low that the detection of one photon in one excitation pulse has a low probability as one photon per hundred excitation pulses, typically. During a TCSPC measurement the sample is continuously excited by a pulsed laser source with a pulse duration in the order of picoseconds and high repetition rate. The electronic system measures the delay time of each photon emitted by the sample once triggered by the excitation pulse, building a probability histogram of the photon emitted as a function of time.

Figure 2.1 shows a typical example of TCSPC electronics schematic.^[26] The excitation pulse (LASER) is split in two signals starting the experiment. One signal is sent to a constant fraction discriminator (CFD) which measures accurately the arrival time of the pulse (start), the other excites the sample (S) and is sent to another CFD which triggers the end time of the signal (stop). Afterwards, a time-to-amplitude converter (TAC) converts the temporal difference between start and stop signals into electrical signals to be processed by the cascade electronics. It measures the time interval between the two signals generating a voltage ramp that increases linearly with the time as function of the difference between start and stop signals. Finally, the voltage ramp signal is amplified by a programmable gain amplifier (PGA) and converted to a numerical value by the analogue-to-digital converter (ADC).



Figure 2.1: Electronics scheme for TCSPC (Principle of Fluorescence Spectroscopy, Lakowicz, Spinger).^[26]

In order to minimize false readings the signal is restricted to a given range of voltages. If the signal is not within this range the event is suppressed by a window discriminator (WD) and the voltage is converted to a digital value which is stored as a single event with the measured time delay. TCSPC records signals with a time resolution of ~150 ps and for short lifetimes (close to the instrument resolution) the use of its instrument response function (IRF) is necessary to deconvolute the actual signal. The IRF contains the width of the excitation pulse, but also consider the temporal dispersion in the optical path and the uncertainty in the timing of the light signal.

In this thesis we used an Edinburgh Instruments F980 TCSPC (time resolution ~150 ps) by exciting with a *ps*-pulsed diode laser (pulse duration = 40 ps, λ_{exc} = 375 nm) and detecting with a cooled photomultiplier tube coupled with a monochromator.

Time-resolved PL measurements were repeated at the Italian Institute of Technology, Milan, using a femtosecond laser source Ti:Sapphire laser (Coherent Chamaleon Ultra II, pulse bandwidth ~100 fs, repetition rate of 80 MHz, and power < 1 nW), useful to pump a secondharmonic crystal (barium borate) and tune the pump wavelength to 470 nm, coupled to a streak camera detection system (Hamamatsu C5680).

Morphological characterization of PDPV. Surface morphology has been investigated by using atomic force microscopy (AFM, Dimension Icon). All AFM images were recorded using tapping mode in air.

2.3 Optical and morphological properties

2.3.1 Absorption and photoluminescence spectra

In Figure 2.2, the chemical structure of *poly*(*4-4'-diphenylene diphenylenevinylene*), or briefly PDPV is shown. PDPV is a phenylated derivative of PPV, having the vinylic hydrogen atoms substituted with phenyl rings. The optical absorption spectra of PDPV in solution (dashed

black line) and in solid-state film spin cast onto fused silica substrates (solid black line) exhibit the lowest energy band peaking at 355 nm. The absorption spectrum of the solid state film has a larger contribution of scattering above 500 nm than the solution spectrum.

The PL spectra of PDPV in solution (dashed red line) and in solid-state film (solid red line) have been normalised to their PL efficiency and the PL spectrum in solution magnified in order to show its features. Both the PL spectra are featureless with a full width half maximum of about 100 nm. Specifically, we estimated the PL efficiency of the dilute solution (poorly emissive) to be as low as ~1%, while, in solid-state film, PDPV has a very high PL efficiency ($\eta_{film} = 51 \pm 5\%$), similarly to what has been reported in [101]. The PL spectrum in the thin film peaks at ca. 520 nm with a characteristic Stokes' shift of about 165 nm, as already observed in literature,^[101] and is blue-shifted with respect to the solution (~15 nm). Such a blue shift is the result of the aggregation, thus in solution, as PDPV is not aggregated, lateral phenyls are free to move and planarise the molecule in the excited state determining a shift of the emission at higher energies.



Figure 2.2: Normalised absorption spectra of PDPV in solution (dashed black line) and in solid-state thin film spin cast onto fused silica substrates (solid black line) and normalised PL spectra of PDPV in solution (dashed red line) and in solid-state thin film spin cast onto fused silica substrates (solid red line). PDPV PL spectrum in solution has been magnified by fifty-one times. The inset shows the chemical structure of PDPV.

Nevertheless, the effect of the restrictions of lateral phenyls can be investigated also with the trend of PL intensity as function of the temperature. In fact as reported in [105] for *poly*(*1,3- phenylene diphenylene*) at room temperature the degree of freedom of the lateral phenyl groups enables a geometrical relaxation to the most favourable configuration but cooling the solid-state sample below room temperature this conformational freedom is decreased, hence the emission occurs at higher energies. In Figure 2.3a, I report similar results for PDPV PL intensity measuring a solid state film spun on spectrosil at room temperature and upon cooling down the sample until 7 K as excited at 375 nm. As shown in Figure 2.3b, by decreasing the temperature of the chamber down to 7 K, a blue shift of the PL peak is measured, starting from 520 nm at room temperature to 505 nm at 7 K, thus the rate is -0.05 nm/K (or -0.24 meV/K) on average, which is in the same order of the values previously reported for PPV in [108]. Simultaneously the full width at half maximum slightly decreases from 120 \pm 1 nm at room temperature to 109 \pm 1 nm at 7 K.

The blue shift reported here for PDPV, similarly to the trend measured for $poly(1,3-phenylene diphenylene)^{[105]}$, is opposite to the usual trend of PL intensity peak as function of the temperature for non-AIE conjugated polymers. For AIE polymers aggregation and decreased temperature concurrently restrict the tendency of the chains to planarise in the excited state, hence leading to emission at higher energies at low temperature. Indeed, the planarization is driven by a lower energy for the planarised molecule. Thus, the higher is the temperature, the wider are the molecular movements which allow the chains a geometrical relaxation towards the most favourable configuration, therefore to emit at lower energies.



Figure 2.3: (a) Photoluminescence spectra of a thin film of PDPV spun on spectrosil at room temperature and upon cooling down the sample until 7 K, as excited by a diode laser emitting at 375 nm and normalized at the PL spectrum collected at 7 K. (b) Shift of the PL peak wavelength of PDPV as function of the temperature.

2.3.2 Titration experiments

To verify if the AIE effect is responsible for such an increase of η from solution to solidstate, I carried out a titration experiment, by measuring the variation of the PL of PDPV in solution at increasing concentration of a non-solvent, which would induce aggregation of the polymeric chains. As we have stated above, PDPV emits weakly in a good solvent such as toluene, therefore we added increasing amount of 2-propanol (IPA, non-solvent for PDPV and well-miscible with toluene) to its toluene solutions, where I kept the final concentration of the mixture constant.

First, absorbance spectra of toluene:IPA mixtures were measured at room temperature and derived molar extinction coefficients, ε , are shown in Figure 2.4. The molar extinction coefficient measures how strongly a chemical species absorbs light at a given wavelength and is proportional to the absorbance (*A*) through the Beer-Lambert law ($A = \varepsilon cl$ where *c* is the concentration of the species in solution and *l* is the pathlength of the absorbed light). Solutions with final concentration fixed at 5×10^{-3} mg/ml progressively change toluene:IPA ratio and show a trend for the peak absorbance wavelength which is not monotonic as function of the IPA content. Indeed, up to 20% volume content of IPA there is no major difference in the absorbance spectra, hence in the molar extinction coefficient. Starting from volume content of IPA larger than 30% the formation of aggregates in mixture induce a red shift of the lowest energy peak of ~30 nm. As aggregates increase in their size the light scatters more evidently and it becomes difficult to distinguish with the sake of certainty the scattering contribution and the actual absorption peak. Nevertheless, aggregates for the mixture with the highest fraction of IPA appear to suffer less the scattering of light at higher wavelengths as confirmed by their size which is visibly smaller at human eye compared to the 50:50 mixture. However, fluorescence measurements obtained by means of a confocal optical microscope have not allowed the measurement of the actual size of PDPV aggregates due to physical limits of diffraction (resolution ~ 200 nm).



Figure 2.4: Molar extinction coefficient, ε , of PDPV in toluene:IPA solutions at room temperature (data not corrected for reflection). Solutions have been obtained by keeping the concentration of PDPV fixed at $5x10^{-3}$ mg/ml and varying the volume ratio between toluene and IPA. Aggregates induce a bathochromic shift of ~30 nm of the lowest energy peak when the IPA fraction rises up to 50%. At increasing IPA volume fraction, the aggregates in solution are bigger and scatter the light significantly at higher wavelengths, inducing a widening in the lowest-energy absorption band and making difficult to distinguish the scattering contribution from the absorbance.

In Figure 2.5a, I show the PL spectra of toluene/IPA (solvent/non-solvent) mixtures with final concentration fixed at $5x10^{-2}$ mg/ml, excited at 375 nm, for increasing volume content of IPA, from 0% peaking at 528 nm to 99% where a 11 nm-blue shift with respect to the non- aggregated solution occurs and the PL spectrum peaks at 517 nm. The PL spectrum of PDPV raises slightly until the IPA fraction in the mixtures reaches 30% and, then, increases steeply beyond 50% IPA content in the mixture, as the non-solvent causes the polymer to aggregate, inducing more efficient emission.

To have a quantitative picture, I measured PL efficiencies, η , for all the toluene/IPA mixtures as reported in Figure 2.5b. Indeed, η is $1.0 \pm 0.1\%$ for the toluene solution, as stated previously in comparison with the thin film, and remains almost unchanged for up-to-20% IPA is added to the toluene solution. Then, η rises to $15 \pm 2\%$, when IPA content is 30% in the mixture, and PDPV starts to aggregate substantially for an IPA fraction of 50% (aggregates are clearly visible by eyes), for which η is ~43 ± 4%. Finally, when the IPA fraction exceeds 70%, η reaches a saturation value close to $60 \pm 6\%$, ~60 times higher if compared with pure toluene solutions.



Figure 2.5: (a) PL spectra (excitation energy, $\lambda_{exc} = 375$ nm) of PDPV in toluene/IPA mixtures with different IPA volume fractions. PDPV concentration is kept constant at 5×10^{-2} mg/ml. (b) PL efficiency, η , of toluene/IPA mixtures as function of the increasing IPA fraction in the mixture. Pictures of the mixtures, taken with the same exposure time, reveal the strong enhancement of the PL as aggregates are generated by the addition of non-solvent.

Furthermore, as an additional confirmation of the beneficial effect of aggregation on emission, we note that solutions of PDPV in toluene with concentrations as low as 5×10^{-3} mg/ml are less emissive than the 5×10^{-2} mg/ml concentrated solution, shown in Figure 2.5, with η values below 1%. We also measured η for solutions with increasing concentration of PDPV in toluene, spanning from 0.1 mg/ml to 10 mg/ml, as for thin films in Figure 2.2. As shown in Table 1, independently from the PDPV concentration in solution, η remains unchanged at ~1%, which appears to be a saturation value for toluene solutions. Similarly, increasing the concentration of PDPV from 0.1 mg/ml to 10 mg/ml in solutions with 1:99 ratio between toluene and IPA, despite the formation of mm-scale aggregates, η is ~ 60%, unchanged as for the mixture in Figure 2.5b (concentration 5×10^{-2} mg/ml). Therefore, considering the extreme ratios of toluene/IPA in the mixture, namely 100:0 and 1:99, a higher concentration of PDPV in solution is not beneficial to restrict further intramolecular rotations.

Concentration (mg/ml)	IPA volume content = 0%	IPA volume content = 99%
5x10 ⁻³	0.8 ± 0.1	61.2 ± 7.5
5x10 ⁻²	1.0 ± 0.1	60.7 ± 5.9
10-1	1.1 ± 0.1	61.0 ± 5.8
1	0.9 ± 0.2	60.5 ± 6.1
10	1.0 ± 0.2	60.0 ± 6.5

Table 1: Measured PL QY of PDPV in toluene solutions (IPA volume content 0%) and toluene/IPA mixtures (IPA volume content 99%), as function of the PDPV concentration from 5×10^{-3} to 10 mg/ml.

2.3.3 Lifetime measurements

Clearly, the formation of aggregates, upon non-solvent addition, boosts the photoluminescence of the polymer, but to gain a further insight into the photophysics of the aggregation-induced emission process for PDPV, I carried out time-resolved PL measurements at

520 nm, *i.e.* about the peak of the PL spectrum of PDPV in the solid-state film shown in Figure 2.5b and obtained by exciting at 375 nm. In Figure 2.6, I present the temporal evolution of the PDPV PL in toluene/IPA mixtures, for increasing volume content of IPA, from 0% to 99%. Interestingly, the temporal evolution of the PDPV PL extends significantly adding non-solvent to the mixture. In analogy to what observed previously by Winroth et al. [109], the PL decay of PDPV in solid-state follows a multi-exponential kinetics. Namely, we had to use a triple exponential expression, $I(t) = A + B_1 e^{-\frac{t}{\tau_1}} + B_2 e^{-\frac{t}{\tau_2}} + B_3 e^{-\frac{t}{\tau_3}}$, to fit globally all the PL decays (global $\chi^2 < 1.4$, fitting curves in red in Figure 2.6) reconvoluted with the instrument response function, keeping the lifetime values (τ_1 , τ_2 , τ_3) linked and leaving the amplitude of each component (B_1 , B_2 , B_3) not fixed. I obtained the best fit for the following decay times: $\tau_1 = 0.15$ ns, $\tau_2 = 1.29$ ns and $\tau_3 = 3.37$ ns. Amplitudes, B_x , and relative contributions of each emissive species; I_x , are shown in Table 2 (coefficient A is the background noise). I calculate I_x as per Eq. (2.1) considering *n* emissive species:

$$\mathbf{I}_{\mathbf{x}} = \frac{\mathbf{B}_{\mathbf{x}} \mathbf{\tau}_{\mathbf{x}}}{\sum_{\mathbf{x}=1}^{n} \mathbf{B}_{\mathbf{x}} \mathbf{\tau}_{\mathbf{x}}}$$
(2.1)

The presence of multiple species for AIE molecules has been already investigated in the literature with femtosecond spectroscopy.^[110] I found that the minimum number of emitting species enabling the global fit of all the PDPV solutions here measured is three. The longer decay times (τ_2 and τ_3) can be ascribed respectively to *intramolecular* singlet exciton and *intermolecular* aggregate states following a common physical model for the luminescence of conjugated polymers.^[52, 111-114] Furthermore, I speculate that the additional component, τ_1 , accounts for a very fast (close to the resolution of our TCSPC unit) recombination decay, dominated by non-radiative processes, which we attribute to the intramolecular rotations of the peripheral phenyl rings, free to move in dilute solutions (with small amount of non-solvent).

The presence of this fast component has been previously observed by ultrafast spectroscopy in [110] and it decreases in percentage as long as the low emissive channel due to the lateral phenyl rings is blocked by the formation of aggregates. The existence of this short

components has been confirmed by ultrafast spectroscopy in collaboration with the group of Prof. Guglielmo Lanzani at the Center for Nano Science and Technology – Italian Institute of Technology (IIT, Milan) measuring emission decays on a 2.4 ns scale, hence improving the resolution up to a few tens of ps. The decay has been fitted with a three exponential equation

 $I(t) = A + B_1 e^{-\frac{t}{\tau_{1f}}} + B_2 e^{-\frac{t}{\tau_{2f}}} + B_3 e^{-\frac{t}{\tau_{3f}}}$ whose parameters are reported in the table. As shown in Figure 2.7, keeping the longest component fixed at $\tau_{3f} = 1.29$ ns, the better resolution of the streak camera enables the measurement of the above-mentioned $\tau_{2f} = 150$ ps component together with another sub-100 ps component ($\tau_{1f} \sim 50$ ps) whose weight decreases substantially when aggregates are formed. As result of the presence of these (fast) emissive species, the temporal decays of mixtures with IPA content up to 20% are clearly shorter, as well as their η are the smallest of the titration series, as shown in Figure 2.5b.



Figure 2.6: Experimental PL decays of PDPV (black lines) in toluene/IPA mixtures for increasing volume content of IPA (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 50%, (f) 70%, (g) 90%, (h) 99% and their correspondent fittings (red lines). Each spectrum has been collected at 520 nm, by exciting the sample at 375 nm. The bumping feature at ~2 ns for the lifetime decays of mixture with IPA content from 0% to 20%, namely the least emissive samples, is related to the response function of the instrument and taken into account in the reconvolution fit.

Table 2: Amplitudes (B_1 , B_2 , B_3) and relative contributions (I_1 , I_2 , I_3) in percentage of the three emissive species, derived by the global fit of the temporal decays of PDPV PL at 520 nm for eight toluene/IPA ratios as reported in Figure 2.6. The expression which has been fitted is $I(t) = A + B_1 e^{-\frac{t}{\tau_1}} + B_2 e^{-\frac{t}{\tau_2}} + B_3 e^{-\frac{t}{\tau_3}}$, converged for $\tau_1 = 0.15$ ns, $\tau_2 = 1.29$ ns and $\tau_3 = 3.37$ ns ($\chi^2 \sim 1.4$) with A being the background noise of the measurement, here not reported.

Toluene:IPA	B ₁	B ₂	B ₃	I ₁ (%)	I ₂ (%)	I ₃ (%)	χ^2
100:0	1.5756	0.0193	0.0008	88.6	10.3	1.1	1.80
90:10	0.9375	0.0116	0.0003	88.9	10.5	0.6	1.67
80:20	0.6166	0.0228	0.0001	73.9	25.9	0.2	1.66
70:30	0.0351	0.0195	0.0059	12.3	64.7	23.0	1.59
50:50	0.0060	0.0199	0.0122	1.2	38.1	60.7	1.31
30:70	0.0040	0.0180	0.0163	0.7	29.6	69.7	1.09
10:90	0.0031	0.0139	0.0148	0.6	26.4	73.0	1.20
1:99	0.0050	0.0167	0.0171	0.8	27.0	72.2	1.34



Figure 2.7: PL decay of PDPV in toluene, excited at 405 nm and collected at 520 nm, using a femtosecond laser source Ti:Sapphire laser (Coherent Chamaleon Ultra II, pulse bandwidth ~100 fs, repetition rate of 80 MHz, and power < 1 nW), useful to pump a second-harmonic crystal (barium borate) and tune the pump wavelength to 470 nm, coupled to a streak camera detection system (Hamamatsu C5680). The decay has been fitted with a three exponential equation $I(t) = A + B_1 e^{-\frac{t}{\tau_{1f}}} + B_2 e^{-\frac{t}{\tau_{2f}}} + B_3 e^{-\frac{t}{\tau_{3f}}}$ whose parameters are reported in the table (A = 0.002) keeping fixed the longest component at $\tau_{3f} = 1.3$ ns = τ_2 as per global fit results in Table 2. These measurements were taken at the IIT - Center for Nano Science and Technology together with Dr. Giuseppe M. Paternò, Dr. Egle Motolokaite, Prof. Cosimo D'Andrea and Prof. Guglielmo Lanzani.

To support more quantitatively our hypothesis and for the sake of simplicity in Figure 2.8a, I plot the relative contribution, I_x , of the three longer emissive species to the PL decays as per our fitting procedure described above, as a function of the increasing IPA volume in the mixtures. Interestingly as per Table 2, the fastest component I_1 is predominant (close to 90%) when the mixture is composed mostly by toluene (IPA ~ 10%) and decreases dramatically as the IPA volume increases and AIE is activated, becoming negligible beyond 50% IPA content. By contrast, the longest component I_3 , which we attribute to aggregates weighs for less than 3% up to 20% volume of IPA and rises abruptly as aggregates are formed by the addition of the non-solvent, reaching a saturation value of about 70% when the ratio toluene/IPA is 30/70, in total similarity to the trend of η , shown in Figure 2.5b. Furthermore, the contribution of the second component I_2 lies between the other two curves reaching its peak (~60%), when the volume of IPA is 30% in the mixture, and saturating at about 30% beyond 70% IPA content.

In addition to this, to unequivocally demonstrate that the enhancement of PDPV emission from the aggregates can be ascribed to the suppression of the non-radiative decay channels, radiative (k_R) and non-radiative (k_{NR}) exciton recombination rates must be extracted. In principle, a straightforward way to obtain such rates is to combine the η and PL lifetime results, and thereby by using the relations in Eq. (2.2)^[68]

$$k_R = \frac{\eta}{\tau}; k_{NR} = k_R \frac{1-\eta}{\eta} \tag{2.2}$$

However, I point out that the above reasoning applies only when a single species is responsible for emission or, in a more complex system, one of the emissive components clearly prevails over the others. In our case, as per our global fit results, none of the above situations is verified, especially above 20% of IPA loading, at which both I_2 and I_3 contribute markedly to the total emission. Therefore, to circumvent this problem, we built our interpretation by considering an average PL lifetime, in analogy to previous reports,^[26, 109] which I calculated as follows:

$$\langle \mathbf{\tau} \rangle = \mathbf{I}_1 \mathbf{\tau}_1 + \mathbf{I}_2 \mathbf{\tau}_2 + \mathbf{I}_3 \mathbf{\tau}_3 \tag{2.3}$$

with $\langle \tau \rangle$ corresponding the average PL lifetime weighted on the relative contributions of the emissive species, I_x , reported in Table 2. $\langle \tau \rangle$ is about 0.3 ns up to 10% IPA content in the solution, increases by a factor of five when the ratio toluene/IPA is 70/30 and, finally, reaches a value of ~2.8 ns for 99% volume of IPA in the mixture.

Most importantly, by substituting $\langle \tau \rangle$ into Eq. (2.2), I derive the effective radiative rate, $\langle k_R \rangle$, and non-radiative rate, $\langle k_{NR} \rangle$. In Figure 2.8b, I also report the calculated effective $\langle k_R \rangle$ and $\langle k_{NR} \rangle$ as function of the IPA content in the mixture. Clearly, whereas $\langle k_R \rangle$ is slightly increasing (less than seven times from 0% to 99% of IPA fraction), $\langle k_{NR} \rangle$ drops dramatically (from 32.7x10⁸ s⁻¹ to 1.4x10⁸ s⁻¹ from 0% to 99% of IPA fraction) as IPA forms emissive aggregates, due to the restriction of the intramolecular rotations, which contribute significantly to non-radiative relaxations in the pure toluene solution. As result of the increasing presence of aggregates, $\langle k_{NR} \rangle$ becomes even smaller than $\langle k_R \rangle$ for mixtures with IPA beyond 70%. Despite the relative simplicity of the model used to calculate radiative and non-radiative rates, the estimation of the $\langle k_{NR} \rangle$ drop of about 96% upon aggregates formation, juxtaposed to the increase of η , constitutes the demonstration of aggregation-induced emission behaviour of PDPV.



Figure 2.8: (a) Relative contribute of the three emissive species, I_x , to the PDPV PL radiative decay as function of the increasing IPA fraction in the mixture toluene/IPA. The three lifetime values result from a global fit of the lifetime decays in Figure 2.6. (b) PL lifetime of PDPV weighted on the three emissive species contributes (I_x) derived from the fit and calculated radiative (k_R) and non-radiative (k_{NR}) rates of PDPV as function of the increasing IPA fraction in the mixture toluene/IPA. All rates were obtained by the model proposed in the text.

2.3.4 Morphology

The effect of the induction of aggregates in the solvent/non-solvent mixtures on the nonradiative rates is remarkable. On the other hand, upon the addition of IPA, the size of the generated aggregates also grows considerably, as clearly visible by eyes, when the fraction of IPA in the mixture exceeds 50%. Spin casting the toluene/IPA mixtures concentrated at $5x10^{-2}$ mg/ml, onto fused silica substrates, we studied the surface morphology of these (very) thin films of PDPV by atomic force microscopy (AFM) to measure the size of the aggregates. Figure 2.10 shows representative images of $2x2 \,\mu\text{m}^2$ areas for PDPV in mixtures with up-to-50% fraction of IPA. At 0% IPA content (a), the film exhibits a very smooth morphology. On the same *z*-scale (7.3 nm, Figure 2.10(a-d)), aggregates emerge significantly and the ratio between their volume and their surface increases, creating a tangled network in the micrometric scale, when the IPA volume reaches the 30% in the solution (d) in correspondence to the activation of the AIE process (between 20% and 30% of IPA). Increasing the volume of IPA, bulky clusters of PDPV aggregates of *ca*. 1 μ m height agglomerate on the edge of the substrate as in (e) without forming a film.



Figure 2.9: AFM height images of PDPV spin cast onto fused silica substrates from mixtures toluene/IPA with IPA content from 0% (a) to 50% (e). All images are on a $2x2 \ \mu m^2$ area.

2.4 Conclusions

I have reported for the first time the full AIE characterisation of a phenylated derivative of PPV, namely PDPV, which increases η of 51 times from the solution to the aggregated solidstate film. The unique combination of PL efficiency and lifetime measurements constitutes a solid method to test the behaviour of AIE materials. For the first time, I measured the photophysical properties of PDPV in solution. Upon the addition of a non-solvent for PDPV, IPA, to the toluene, the η is 60-fold higher and, simultaneously, the PL lifetime is about nine times longer, when IPA content in the mixture is 99%. The latter lowers the non-radiative rates by 96%, demonstrating the AIE feature of PDPV. The lifetime measurements of non-aggregated PDPV in solution have demonstrated the presence of very fast species, which decay non-radiatively due to the unrestricted rotations of lateral phenyls and confirmed the extraordinary solid-state properties of AIE materials which leverage the restriction of intermolecular interactions to boost their PL efficiency.

3 Organic light-emitting diodes with PDPV/PVK blends

3.1 Introduction

In the last three decades polymer light-emitting diodes (PLEDs) have been widely investigated and currently they represent crucial devices for last-generation displays and lighting sources in industry. When active polymers became solution processable the cost of fabrication per device dropped down drastically and lower than inorganic ones, hence suitable for large area production. The basic structure of a PLED is composed by an emissive material sandwiched between a cathode and a transparent anode^[38] and made of multilayers^[115, 116] or blends^[48, 49]. The cathode material is usually Calcium (Ca) while anode the can be poly(3,4-ethylene dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) on top of Indium- Tin-Oxide (ITO).

The working principle of a PLED is explained in Figure 3.1.^[20] The forward bias applied to the PLED structure and opposite to the built-in potential V_{BI} allows the injection of electrons from the cathode and holes from the anode into the emissive layer. The diffusion of charges into the emissive layer proceeds until they get close forming an exciton which can decay radiatively (emitting a photon) or non-radiatively (phonons).

The main figure to quantify the efficiency of a PLED is the external quantum efficiency EQE in Eq. (3.1):

$$EQE = \gamma \eta r_{st} n_{ext}$$
(3.1)

where γ is the exciton formation efficiency per charge injected, η is the photoluminescence efficiency, r_{st} is the singlet to total number of excitons ratio formed in the device (i.e. the amount of excitons that can radiatively decay) and n_{ext} is the optical outcoupling of the emitted light which depends on the refractive index. Eq. (3.1) is valid only for fluorescent materials while for phosphorescent materials also the phosphorescence efficiency of the active layer should be taken into account.^[117] Usual values of EQE span in a range from ~2% to ~30% of the η value, as such a high η is essential to get higher EQE.



Figure 3.1: (a) Before contact with the active polymer characterized by its energy values HOMO-LUMO anode and cathode work functions are $\Phi_{an.}$ and $\Phi_{cath.}$ respectively. (b) Once in contact chemical potential equilibrium creates a potential difference in the active layer known as built-in potential, V_{BI} . (c) When a forward bias is applied to the anode, opposite to V_{BI} , electrons are injected into the emissive layer from the cathode and holes from the anode, forming excitons that can radiatively decay.

As explained in Chapter 2 the strong intermolecular π - π stacking which is conventional in conjugated polymers induces the aggregation-caused quenching (ACQ) limiting their implementation in organic light-emitting diodes (OLEDs). In fact, the emission is often quenched due to the planarity of common organic materials. The introduction of AIE luminogens has been recognized as a powerful approach in order to obtain high solid-state quantum yield, high photostability and no ACQ effect, hence AIE emitters have been proposed as outstanding candidates for OLEDs.^[118] Recently, non-doped OLEDs based on aggregation-induced delayed fluorescence (AIDF) emitters have shown excellent performances with external quantum efficiencies in the same order of magnitude of traditional doped OLEDs (EQE > 10%). ^[119, 120] These results may give a hint for their use in large-scale commercial applications and a range of fields which are limited only by researcher imagination such as sensing and biology.

PDPV is an attractive polymer for emission thanks to its high PL efficiency ($\eta \sim 51\%$), its good solubility in organic solvents and its photostability demonstrated in [109]. First use of PDPV as emitting layer in OLEDs has been reported two decades ago in [101] in combination with *polyvinylcarbazole* (PVK) and *poly(p-phenylene vinylene)* (PPV) in a triple-layer structure with ITO as the anode with luminances in excess of 1300 cd/m², turn-on voltages of ~8 V and internal quantum efficiencies (IQEs) in the range 0.4%-0.8%, ten times higher than for singlelayer PDPV devices. Figure 3.2 shows the energy diagram of the OLED structure reported in [101]. PVK is a non-conjugated polymer with large energy gap which exhibit a good conductive and photoconductive properties due to the pendant conjugated chain and has been used as holeinjection layer due to his favourable HOMO level position. Nevertheless, other studies have reported the increase of PL and EL efficiencies of emissive polymers when in blend with PVK which helps decreasing the ACQ occurrence.



Figure 3.2: Energy level diagram with HOMOs (highest occupied molecular orbitals) and LUMOs (lowest unoccupied molecular orbitals) level positions determined with respect to the vacuum for each material of the OLED structure reported in [101], considered isolated with no electric field applied. The work function of indium tin oxide (ITO), calcium (Ca) and aluminium (Al) is also shown.

Finally, PDPV is remarkably stable and only slightly affected by ageing as assessed more recently in [109]. The optical properties have appeared unchanged after a decade of storage in the dark in powder form and the fabrication of single-layer OLEDs has been reported for a ITO/PEDOT:PSS/PDPV/Ca structure showing characteristic luminance above 800 cd/m² at 10 V with turn-on voltage of ~5.1 V and a maximum EQE of 0.23%, improved compared to the structure in Figure 3.2 due to the better hole injection by the PEDOT:PSS layer which has a work function of -5.2 eV. The maximum EQE of 0.23% agrees well with the maximum IQE of 1.2% for OLEDs in [101] calculated as per Eq. (3.2) where n is the refractive index (~1.5)

$$IQE = 2 \cdot n^2 \cdot EQE \tag{3.2}$$

Eq. (3.2) is valid under the assumption that the dipoles are distributed randomly, hence the emission is spatially homogeneous, and there are no photonic effects (e.g. waveguiding).^[121]

Here, I report the fabrication and optical characterization of OLEDs with blends of PDPV:PVK employed as emissive layer in a typical structure ITO/PEDOT:PSS/active layer/Ca/Al, thus exploiting the presence of PEDOT:PSS to improve the hole injection and the one of PVK in blend to boost the induced aggregation of PDPV demonstrated in Chapter 2.

3.2 Experimental methods

Films preparation. The synthesis of PDPV has been previously reported in [106]. PVK was sourced from Acros Organics with a molecular weight MW = 90,000 and its chemical structure is shown in Figure 3.3. Blends of PDPV and PVK, both dissolved in toluene, were spin cast onto fused silica substrates keeping the concentration of solutions of PDPV and PVK constant at 10 mg/ml and changing the weight ratio between them. The films were deposited in a N_2 environment via spin-coating at 1500 rpm to obtain a thickness ~90 nm, measured with a Dektak profilometer.

Characterization of PDPV films. Optical absorption spectra were measured using an Agilent 8453 UV-Vis spectrophotometer. Photoluminescence was collected from an Andor Shamrock 163 spectrograph coupled with an Andor Newton EMCCD exciting the samples by a ps-pulsed diode laser (pulse duration = 40 ps) emitting at 375 nm. The optical characterization was conducted using an integrating sphere setup.^[107] All absorption and PL spectra were collected in air at room temperature. Time-resolved PL measurements were carried out in air at room temperature with a time-correlated single photon counting (TCSPC) spectrometer (LifeSpec Edinburgh Instruments). Samples were excited at 375 nm with picosecond pulsed diode laser. Surface morphology has been investigated by using atomic force microscopy (AFM, Dimension Icon). All AFM images were recorded using tapping mode in air.

OLEDs fabrication. ITO substrates were cleaned in an ultrasonic bath using acetone and isopropanol, were then dried under a N_2 stream and treated in an O2 plasma chamber for 10 min. A ~50 nm layer of PEDOT:PSS (purchased from Sigma Aldrich) was spin-coated at 5000 rpm from a 2.8 wt% dispersion in water. The active layer was spin-coated from the same solutions used for the PL characterization and a Ca/Al (30/200 nm) cathode was thermally evaporated on top.

OLEDs characterization. OLEDs were measured in air using a Keithley 2400 source meter (USA) for both the current measurement and the voltage supply. A calibrated silicon photodiode was used to measure the emitted light from the OLEDs, while the electroluminescence (EL) spectra were collected with the same spectrophotometer employed for PL experiments.

3.3 Optical and electronic properties

3.3.1 Absorption and photoluminescence spectra

Solid-state films deposited directly by mixtures of toluene and IPA as per the morphology shown in Figure 2.9 do not exhibit the uniformity necessary for their integration into devices. Alternatively, making a blend of PDPV with materials dissolved in non-solvents cannot guarantee smooth morphologies as required for the following deposition of metal contacts when fabricating OLEDs. Thus, I investigate the possibility of raising the PL and EL efficiencies by blending PDPV with PVK and incorporating such active layers within the typical sandwiched-structure of an OLED. PVK acts as matrix for PDPV being a non-conjugated polymer, hence there is no investigation of host-guest strategy in the active layer.

Prior to the integration of these films into devices, I characterized the optical properties of films where the ratio between the two materials is varied in weight from pure PDPV films to 80% w/w PVK in blend with PDPV by four equally-spaced ratios. The absorption spectra of these films are shown in Figure 3.3 in dotted lines exhibiting the lowest energy band peaking at 355 nm which decreases in intensity as long as the PVK absorption band becomes prominent with a clear peak at 346 nm for larger amount of PVK in blends. Correspondingly, the PL spectrum of PDPV peaking at 520 nm for PDPV films as shown in Figure 3.3 (solid lines) remains featureless for every blend and experiences an overall ~10 nm-blue shift for the 20:80 (PDPV-PVK) blend compared to pure PDPV PL spectrum similarly to the change measured for aggregated solution mixtures and can give a hint of the enhanced formation of PDPV aggregates in solid-state matrices due to the simultaneous presence of PVK in blend.



Figure 3.3: Absorption (dotted) and PL (solid) spectra of PDPV spectra in blend with increasing loadings of PVK from 0% to 80%. Chemical structures of PDPV and PVK are shown on the right.

In Table 3 I summarize photoluminescence features of PDPV pure and in blend with increasing loadings of PVK. The peak wavelength of PL spectra moves from 520.1 nm for pure PDPV films to 510.5 nm when the loading of PVK in blend equals 80% for an overall 9.6 nm blue shift. As per PL spectra of PDPV as function of the temperature reported in Figure 2.3, the effect on PDPV concomitant to the increasing loading of PVK in the blend determines an unexpected blue shift of the PL peak due to a possible stiffening of PDPV chains and restriction to phenyls rotations when PVK content increases, hence the emission takes place at lower wavelengths.

Correspondingly, the full width at half maximum (FWHM) of the PL spectrum of PDPV is reduced by ~2% for the 20:80 PDPV:PVK blend when compared to pure PDPV and this effect can be encountered again in relationship with the restricted movements of phenyl rotors due to less room left for their most favourable planar configuration in the excited states. Thus, a small homogeneous effect can be ascribed as the main cause of such a reduction in FWHM. I also report measured values of the PL quantum efficiency, η , for each blend assessing a rise of η by 12% when the concentration of PVK in blend is 40% and a decrease of η at higher concentration of PVK in blend. Indeed, as the PVK loading in blend increases, PVK absorbs more considerably but the overall PL quantum efficiency decreases as PVK is poorly emissive.

Film	λ_{PL} (nm)	FWHM (nm)	η (%)
PDPV	520.1 ± 0.5	118.0 ± 1.0	51.0 ± 1.1
20% PVK	519.7 ± 0.5	118.0 ± 1.0	52.3 ± 1.2
40% PVK	518.2 ± 0.5	117.4 ± 1.0	57.2 ± 1.5
60% PVK	514.8 ± 0.5	117.0 ± 1.0	53.2 ± 1.3
80% PVK	510.5 ± 0.5	115.6 ± 1.0	38.8 ± 1.0

Table 3: Measured PL peak wavelength, full width at half maximum (FWHM) and PL quantum efficiency, η , for PDPV in blend with increasing loadings of PVK from 0% to 80%.

3.3.2 Lifetime measurements

The slightly increased PL quantum efficiency of for the PDPV:PVK 60:40 blend suggests that the photophysics of the film is changing when adding PVK to the blend. Therefore, to have a further insight in the photophysics of the system, I carried out lifetime measurements on the PL decays of PDPV neat and in blend with PVK on the same samples measured in Section 3.3.1 at 520 nm, i.e. about the peak of the PL spectrum of PDPV as per PL plots shown in Figure 3.3 obtained by exciting at 375 nm. In Figure 3.4, I present the temporal evolution of the PDPV PL in solid-state films, pure and in blend with PVK for four equally-spaced weight ratios with their fitting decays overlapped in solid red lines.

Table 4 shows the results of the fits, reporting lifetime values and relative contribution of each species for the five samples here measured. The equation used to fit the PL decays is $I(t) = A + B_1 e^{-\frac{t}{\tau_1}} + B_2 e^{-\frac{t}{\tau_2}}$ as this bi-exponential expression is consistent to minimize the root-mean squared error of the fit. Two species have been clearly detected, i.e. a shorter temporal component (~1.3 ns) which can be attributed to the intramolecular singlet exciton and a longer

temporal component (~3.6 ns) which the lifetime emission from intermolecular aggregate states. Notably these two components are very close to the two longest components measured for the PDPV in toluene/IPA mixtures and I interpret their physical meaning in the same way as explained in Section 2.3.3. However, the higher degree of packing of the polymer chains in solidstate films slightly increases the longest temporal component which depends on the aggregation. Significantly, the shortest component measured in solution with a lifetime of about 150 ps and progressively disappearing for more aggregated PDPV mixtures is not detected in solid-state films PL decays as the rotations of lateral phenyls of PDPV are completely inhibited in the aggregated state.



Figure 3.4: Experimental PL decays of PDPV:PVK films (black lines) for 5 different blending ratios (a) 100:0, (b) 80:20, (c) 60:40, (d) 40:60, (e) 20:80 and their correspondent fits (red). Each spectrum has been collected at 520 nm, exciting the sample at 375 nm.

Table 4: Lifetime values, τ_1 and τ_2 , and relative contributions, I_1 and I_2 , of the two emissive species, obtained by the fit of the temporal decays of PDPV:PVK thin films PL at 520 nm for five weight ratios of PDPV and PVK in blend. The expression which has been fitted is $I(t) = \mathbf{A} + \mathbf{B}_1 \mathbf{e}^{-\frac{t}{\tau_1}} + \mathbf{B}_2 \mathbf{e}^{-\frac{t}{\tau_2}}$.

PDPV:PVK	τ_1 (ns)	I ₁	τ_2 (ns)	I_2 (%)	χ^2
100:0	1.24 ± 0.02	0.26	3.57 ± 0.02	0.74	1.21
80:20	1.34 ± 0.02	0.27	3.69 ± 0.02	0.73	1.14
60:40	1.34 ± 0.02	0.26	3.67 ± 0.02	0.74	1.20
40:60	1.34 ± 0.02	0.26	3.66 ± 0.02	0.74	1.16
20:80	1.33 ± 0.02	0.26	3.62 ± 0.02	0.74	1.19

All the films containing PVK have an average lifetime which is about ~4% higher than neat PDPV. The latter is unusual compared to the lifetime increase for the guest in a blend due to aggregation quenching which decreases the radiative rates. Interestingly, the effect of aggregation quenching on PDPV is minimum, therefore the PL quantum efficiency keeps on increasing before the effect of the poorly emissive PVK becomes predominant.

3.3.3 Morphology

The ease of deposition for solution-processed active layers to be integrated into OLEDs encourages their use for low-cost optoelectronic devices. Nevertheless, it is significantly important to obtain uniform devices to have comparable characteristics in terms of thickness of the active layer and surface roughness, which are crucial for commercial applications. Typical active layers in OLEDs are ~100 nm thick and low roughness is required in order to obtain smooth surfaces where to evaporate good-quality metals to act as cathode.

Spin coating is a very easy and inexpensive technique to deposit solution-processable active layers for OLEDs. When a solution is dropped either onto a glass/silica substrate conveniently treated in order to improve its wettability or on another previously deposited material which cannot be dissolved in the same solvent used for the active layer, a few seconds are enough to obtain largely homogeneous films. In Figure 3.5, I report the height images of PDPV films, neat dissolved in toluene and in blend with poly(9-vinylcarbazole) (PVK), spin cast onto fused silica substrates for three ratios of the two materials, i.e. PDPV:PVK = 100:0, 60:40 and 20:80, by means of tapping-mode atomic force microscopy. The film quality is very high, no holes are present and the surface is smooth with an overall roughness characterised by a root mean square of about 4 nm over $2x2 \mu m^2$ area.



Figure 3.5: Tapping-mode atomic force microscopy (AFM) height images of PDPV films neat dissolved in toluene and in blend with *poly(9-vinylcarbazole)* (PVK). All films were spin cast onto fused silica substrates from mixtures for three different ratios (a) PDPV:PVK = 100:0 (b) PDPV:PVK = 60:40 (c) PDPV:PVK = 20:80. All images are on a $2x2 \ \mu m^2$ area. Blends of PDPV and PVK, both dissolved in toluene, were spin cast keeping the concentration of PDPV and PVK constant at 10 mg/ml and changing the weight ratio between PDPV and PVK. All films appear homogeneous with no phase separation in blends and very low roughness.

3.3.4 OLEDs photoluminescence and electroluminescence spectra

PDPV:PVK blends are interesting candidates to be incorporated into OLEDs considered their high photoluminescence efficiency. I fabricated PDPV OLEDs as per experimental procedure described in Section 3.2. Figure 3.6 shows the photoluminescence (PL) and electroluminescence (EL) spectra of PDPV OLEDs. As PL spectra experience an overall ~9.6 nm-blue shift by comparing the peak wavelength of the 20:80 (PDPV-PVK) blend with the neat PDPV PL spectrum as highlighted in Section 3.3.1, the EL spectra resemble the same trend by a
blue-shift of ~13.8 nm considering the peak wavelength for the two limit ratios of PDPV/PVK in blend. As such EL peak wavelength for neat PDPV OLED is located at 525.9 nm and for 20:80 PDPV:PVK blend at 512.1 nm. As for PL spectra, EL spectra result featureless and no contribution of PVK emission is recorded between 400 and 500 nm.

However, the FWHM of EL spectra is larger than for PL spectra as reported in Section 3.3.1 and reduced by ~10% from neat PDPV (FWHM_{EL} = 132 nm) to 20:80 PDPV:PVK blend (FWHM_{EL} = 120 nm). Indeed, the overall effect of the EL spectra broadening is the shift of the average wavelength to longer wavelengths as in the electroluminescence process the charges are funnelled to the lowest energy states. Nevertheless, the current flowing into the device heats up the active layer releasing some degrees of restrictions of the PDPV chains which may planarise and emit at lower energies for the pure PDPV compared to the PDPV in blend with PVK.



Figure 3.6: PL (solid lines) and EL (dashed lines) spectra of all-investigated OLEDs embedding PDPV as active layer, neat and in blend with PVK. All measurements were carried out at room temperature and the PL spectra obtained exciting by using a pulsed diode laser at 375 nm and hitting the samples from the transparent side of the OLED structure off from the electrodes area.

3.3.5 Current density-Voltage-Luminance curves

In Figure 3.7 I plot the density-voltage-radiance (*JVR*) and external quantum efficiency (*EQE*) versus current density curves, whereas OLEDs features are summarised in Table 5. Interestingly, the turn-on voltage *V*_{ON} which occurs at 5.6 V for pure PDPV decreases by one third for 40% PVK OLED (3.8 V) and is lower for devices containing 20% PVK and 60% PVK devices than for pure PDPV, whereas the turn-on voltage is 6.9 V for the OLED with 80% PVK. Correspondingly, the maximum radiance is 0.38 mW/cm² (~ 2600 cd/m²), 17.5% higher for the most efficient OLED (40% PVK) compared to pure PDPV, for which we measured 0.31 mW/cm², whereas the maximum radiance for higher loadings of PDPV is 0.23 mW/cm² and 0.27 mW/cm², for 60% PVK and 80% PVK OLEDs respectively.

The increase of the measured current density in the 40% PVK OLED, as a driving voltage of 2.5 V is applied, rises the number of free carriers in the device which are able to form the exciton and recombine radiatively. Therefore, the turn-on voltage decreases to 3.8 V for the 40% PVK blend, which is beneficial for the actual operation of the device. As the *EQE* of an OLED is the ratio of emitted photons over generated electrons, a lower V_{ON} requires lower power to drive the device and obtain the desired device efficiency. Indeed, given V_{ON} , I derived the correspondent current density in each OLED from the *JVL* curves, hence the *EQE* value for each device reported in Figure 3.7 as function of the current density. The maximum *EQE* value is located for a current density at least equal to the current density at V_{ON} .

The best efficiency has been measured for the device incorporating as emissive layer the blend with 40% PVK, which was also the most efficient when measured spin cast on a fused silica substrate as per Table 3 and exhibits a maximum *EQE* of 0.33% ($J = 0.002 \text{ mA/cm}^2$), which is 50% higher than what has been measured for pure PDPV ($EQE_{max} = 0.22\%$, $J = 53 \text{ mA/cm}^2$). For the 20% PVK OLED the EQE_{max} is 0.35% at $J = 26 \text{ mA/cm}^2$, for the 60% $EQE_{max} = 0.23\%$ at $J = 18 \text{ mA/cm}^2$ and for the 80% PVK OLED EQE_{max} is 0.27% at $J = 30 \text{ mA/cm}^2$. As such, the lower V_{ON} of the 40% PVK OLEDs definitely enhance its operation at current densities up to four

order of magnitude than in all the other devices. Higher *EQE* values at low current densities cannot be considered as they occur below the V_{ON} , hence where the devices are still off, and result from the ratio between noise and low currents. Nevertheless, the *EQE* averaged over all the fabricated devices is close to 0.15% despite the amount of PVK in the blend. Such *EQE* values for PDPV confirm previously measured pure PDPV OLEDs reported in [109] and remain interesting as we achieved them from solution-processed not optimised devices and using the same batch of PDPV used in [109], certifying the remarkable stability of this material.



Figure 3.7: (a) *JVR* curves and (b) *EQE* as function of current density for PDPV OLEDs pure and in blend with different ratios of PVK. Only values of *EQEs* above the turn-on voltage are real and reported in Table 5.

Sample	V _{ON} (V)	Radiance (mW/cm ²)	EQE _{max} (%)	EQE _{av} (%)
PDPV	5.6	0.31	0.22	0.14 ± 0.06
20% PVK	5.0	0.35	0.28	0.16 ± 0.08
40% PVK	3.8	0.38	0.33	0.14 ± 0.05
60% PVK	5.0	0.23	0.21	0.15 ± 0.06
80% PVK	6.9	0.27	0.20	0.12 ± 0.07

 Table 5: Summary of OLEDs characteristics of PDPV:PVK OLEDs.

3.4 Conclusions

In conclusion, I reported the full optical characterization of PDPV in blend with PVK using an approach never used before for the same material increasing its PL efficiency by ~12% for the most efficient ratio in PDPV:PVK blend. Due to the high solid state efficiency of PDPV, I show performance of OLEDs embedding PDPV and blends of PDPV and PVK and attaining *EQE* values improved by 50% for a 40% PVK loaded active layer compared to pure PDPV with lower turn-on voltage and higher radiances.

4 Solution-processed 1D photonic crystals doped with PDPV

4.1 Introduction

A general introduction on 1D photonic crystals (PhCs) in Section 1.4.1 has shown the main characteristics of these photonic structures which have become relevant for their applications for light management, photovoltaics, sensing and lasing. Here, I go a step forward dealing with 1D all-polymer microcavities, which reduce the traditional costs of lithographic techniques required by inorganic PhCs and pave the way towards low-cost mass scale production.

1D PhCs are multi-layered planar structure which exhibit a periodicity in one direction as shown in Figure 1.9. Artificial PhCs resemble natural structures such as the mother of pearl^[122] and the *Pollia Condensata* skin^[123], which is reported in Figure 4.1a and whose astonishing light blue is given by an underlying multi-layered organization. The interest in all-polymer PhCs is related to their emulation of nature adding the peculiarity of full flexibility if compared to inorganic structures as shown in Figure 4.1b^[124] enabling the fabrication of full flexible arrays of lasers. Nevertheless, the advantage of low cost for large area production and the diversified chromatic response can be usefully combined and used for functional architecture which is becoming a hot topic recently as shown in Figure 4.1c.^[125]



Figure 4.1: (a) Pollia Condensata berries^[123] have their typical light blue colour given by their periodic underlying structure. (b) Flexible all-polymer microcavity optically pumped in the blue region of the visible spectrum.^[124] (c) Coloured plastic panels used for functional architecture.^[125]

Among the wide range of applications of 1D PhCs, in this chapter I will focus on the use of all-polymer microcavities for light management. Researchers have deeply worked for new solution-based and large-area (modules up to ~100 cm²) fabrications, trying to make even more appealing a laboratory process which is applicable to industry. In the literature, the use of a microcavity structure to enhance the PL of fluorescent polymers was proved by employing metallic mirrors alongside inorganic DBRs.^[126] Conjugated polymers were already being considered as viable candidates for large area displays, however, their broad emission spectrum was unable to meet the technical requirements for displays, thus a method for narrowing the PL spectrum of these polymers was required.

The first attempt, consisting of the fabrication of a DBR and a metal as mirrors for the cavity structure, resulted in narrowing the PL full width at half maximum (FWHM) of *poly*(*2,5- dialkoxy-phenylenevinylene*) from 128 nm to 16 nm.^[126] Later, thanks to their improved reflectivity and lower absorption, the use of inorganic DBRs to replace the metallic mirrors was demonstrated beneficial to the PL enhancement in microcavities. *Poly*(*para-phenylenevinylene*) (PPV) was investigated with PL enhancement factors of two orders of magnitude and the FWHM of the PL spectrum narrowing to ~18nm for DBR/PPV/DBR.^[127] Lasing features were also observed in conjugated polymer microcavities with thresholds of only 15 µJcm⁻² providing motivations for the possible fabrication of organic lasers.^[128]

A further advancement for low-cost and large-scale application of microcavities occurred when inorganic DBRs were replaced with polymeric DBRs. Polymers were used for DBRs as they are significantly cheaper and easier to handle. The realization of organic DBRs employed the method of spin coating, which allows for simple tuning of the layer thicknesses by altering the spin speed and/or the concentration of the solutions. In one of the first studies of this nature, cellulose acetate (CA) and polystyrene (PS) were used to fabricate an all-polymer microcavity embedding *poly*(*9*,*9-dioctylfluorenyl-2*,*7-diyl-co-1*,*4-benzo-(2*,*1'-3)-thiadiazole*) (F8BT) as an active material.^[124] CA and PS were chosen as they are cheap and soluble in orthogonal solvents, thus allowing them to be easily layered on top of one another with little risk of percolation, which would result in detrimental effects to the optical quality of the photonic structure. However, as

the refractive index difference between CA and PS is quite small, the resultant DBR stop band which depends on the refractive index contrast as shown in Eq. 1.3 was quite narrow (~25 nm) and only suppressed a small portion of the PL spectrum of the active layer. A later study tackled this limitation employing *polyvinylcarbazole* (PVK) as high refractive index material ($n_{PVK} > n_{PS}$) to create a DBR with a 50 nm-wide stop band.^[77] All-polymeric microcavities have been reported with high quality factors as of 80-180 and also had lasing thresholds of <20 µJcm⁻², which is comparable to their counterparts using inorganic mirrors.

These results have renewed interest towards the fabrication of devices that have applications in low-threshold lasing devices and sensing equipment similar to those already demonstrated by inorganic structures.^[129-131] Furthermore, due to the optical resonance features of the cavity, microcavity devices can also be used to probe some of the intricacies of quantum mechanics such as strong coupling and the Purcell Effect.^[132]

Development in this field involves the fabrication of tuneable microcavities ^[133, 134] and further applications in polymer-based solar cells.^[135] One of the most important commercial implications of microcavity research is the development of low cost and highly sensitive sensors. Recently, several groups have made breakthroughs in development of all-polymeric photonic crystals for vapour sensing, suggesting that widespread use of such devices is of high interest.^[136] Other advances in microcavity development include the use of nanocrystals dopants to create microcavities with quality factors up to 250^[95] as well as the use of polymeric DBRs alongside perovskite materials to pave the way to new applications in hybrid optoelectronics.^[137]

4.2 Experimental methods

Fabrication of PDPV microcavities. Polyvinylcarbazole (PVK, Mw = 90,000) and cellulose acetate (CA, $Mw = 61\ 000$) has been used for multilayer growth as high refractive index material and low refractive index material, respectively. PVK was sourced from Acros Organics and CA was purchased from Sigma Aldrich and used without further purification.

Poly(4,4'- *diphenylened iphenylvinylene*) (PDPV, Mw = 28,100) was synthesised as previously reported in [98] and employed as active layer in microcavity. Toluene and diacetonalcohol (4- *hydroxy-4-methyl-2-penthanon*) were used to prepare polymer solutions with a concentration of 25 mg/ml for PVK and 23 mg/ml for CA. The deposition of PVK:CA DBRs was performed by spin-coating (Süss Microtech Lithograghy GmbH AK200169) over glass substrates in laboratory environment without temperature or humidity control. Only for PVK layers, a further annealing process of 60 s at 70 °C on a hot plate was added to ensure the layer was completely dry. Layer thickness was selected by changing the spinning speed and solution concentrations. The samples analysed in this work were made of 25 bilayers DBRs with nominal thicknesses 80 and 90 nm for PVK and CA layers, respectively, chosen as per design illustrated in Section 4.3.1 and measured using a Dektak³ profilometer from Veeco Instruments. The PDPV microcavity was obtained by spinning a PDPV toluene solution (15 mg/ml) over a multilayer made of 25 bilayers PVK-CA films at 800 rpm. Then, an additional 25 CA-PVK bilayers were grown over the PDPV film to complete the structure, as shown in Figure 4.2. The total transverse size of the microcavity structure is about 8.5 µm.

Optical characterization of PDPV microcavities. Absorption spectra of PDPV were collected using an Agilent 8453 UV-Vis spectrometer. Sample uniformity and thickness check over the area of the whole microcavity (2x2 cm²) has been performed by illuminating the samples with an Ocean Optics halogen lamp normally to the surface of the structure while an Andor Technology EMCCD (SR1 631) spectrometer has been used to measure the transmittance spectra. Angle-resolved transmittance spectra for both *S*- and *P*-polarizations were measured with the same setup above by positioning the samples on a mobile goniometer and turning the sample at 5° steps. Angle-resolved PL spectra were collected with a setup consisting of an excitation source such as a *ps*-pulsed diode laser (pulse duration = 40 ps, λ_{exc} = 375 nm) hitting on the sample at a fixed angle of 10° from the sample plane and an Andor Technology EMCCD (SR1 631) spectrometer placed normal to the sample and then moved with increments of 5°, such that only photons from PL directional contributions at variable collection angles are measured, off from the

reflection of the laser. The PL efficiency has been measured by means of an integrating sphere exciting the samples at 375 nm following the method described by de Mello.^[107] Time-resolved PL measurements were carried out exciting with a *ps*-pulsed diode laser (pulse duration = 40 ps, $\lambda_{exc} = 375$ nm) and detecting the PL with a photomultiplier coupled to a monochromator and a time-correlated single-photon counting unit (TCSPC, Edinburgh instruments, LifeSPec II, time resolution ~150 ps).



Figure 4.2: Schematic of a microcavity structure consisting of 2 DBRs of 25 PVK:CA bilayers each incorporating an active layer of PDPV in the centre of the structure.

4.3 Optical characterization

4.3.1 Design of DBRs

As described in Section 1.4.1, the effective fabrication of a microcavity requires the stop band of the constituting DBRs overlapping the emission spectrum of the active layer within the cavity. The position and depth of the stop band can be modified by changing the thicknesses and/or the refractive indices of each layer as well as the number of bilayers in a given device as represented in Section 1.4.1. In order to determine the ideal thicknesses of each layer in each DBR, the Transfer Matrix Method (TMM) has been employed to model the optical transmittance of each mirror as detailed by Bellingeri.^[138]

The TMM is a method used to predict the propagation of electromagnetic waves through a stratified medium. The Fresnel equations describe the reflection and transmission of light from a single interface. When multiple interfaces exist, the reflections are partially transmitted and reflected through each layer, creating patterns of constructive and destructive interferences. The TMM script, developed in the group by Prof. Francesco Scotognella at Department of Physics of the Politecnico di Milano and here used, takes into account the multiple reflections and transmissions from one layer to the next of the DBR, describing each layer by four coefficients (a 2x2 matrix) depending on Fresnel equations. The whole DBR is described by the product of the individual layer matrices.^[138] I enhanced the TMM code by substituting a wavelengthdispersive relation for the refractive index of each layer derived for commercial materials by Bellingeri^[138] to have more accurate results in any range of the considered spectrum.

Being the PDPV PL spectrum already measured as per Figure 2.2, the design of the DBR consisted in the choice of the correct PVK and CA thicknesses to realize a $\lambda/4$ DBR centred at ~530 nm, hence to obtain an excellent overlap with PDPV maximum fluorescence. Therefore, the design of the microcavity mirrors was simulated by using refractive index dispersions described via the Sellmeier equation (Eq. 4.1) for PVK and CA allowing for a first rough evaluation of DBR films thicknesses useful to determine the $\lambda/4$ condition, which can then be finely tuned by slightly modifying the spinning speed in the fabrication process:

$$\mathbf{n}^2 - \mathbf{1} = \frac{A\lambda^2}{\lambda^2 - B^2} + \frac{C\lambda^2}{\lambda^2 - D^2} + \frac{E\lambda^2}{\lambda^2 - F^2} \tag{4.1}$$

where *n* is the refractive index, λ is wavelength and constants *A*-*F* are characteristic of the material. Coefficients *A*-*F* reported by Bellingeri^[138] for a wide range of commercially available polymers, including PVK and CA, are useful for constructing a dispersion relation for the refractive index of a chosen material. The wavelength-dependent refractive indices for PVK and CA as calculated via (4.1) are shown in Figure 4.3. Comparing the refractive indices of PVK and

CA at 530 nm shows a difference of 0.193, which is quite large with respect to other combinations of commercially available polymers.



Figure 4.3: Refractive index, n, of PVK (a) and CA (b) as function of the wavelength in visible and nearinfrared spectrum ranges, as derived by using Sellmeier equation (Eq. 4.1) and coefficients *A*-*F* as reported in [138]. The refractive index at 530 nm for both materials has been highlighted and can be used for rough approximation of the optical path of the light within each layer.

Known the approximated values of the refractive index for PVK and CA at 530 nm, by using Eq 1.1, I calculated a bilayer thickness, d, of ~170 nm to meet the $\lambda/4$ conditions. Furthermore, as per requested optical path in each layer of the DBR to be similar in order to allow maximum constructive interference, such that $d = n_{PVK}d_{PVK} + n_{CA}d_{CA}$, it results that the best thickness which satisfy this condition are $d_{PVK} = 80$ nm and $d_{CA} = 90$ nm. Using these simple equations, as increasing the number of bilayers affects the depth of the stop band, I calculated how the stop band of PVK:CA DBRs is expected to change as function of the number of bilayers using the Transfer Matrix Method (TMM). For an overall bilayer thickness of 170 nm $(d_{PVK} = 80 \text{ nm and } d_{CA} = 90 \text{ nm})$, a number of bilayers included between 20 and 30 is able to guarantee a depth in transmittance close to unity. For the results reported in this thesis DBRs 25bilayers thick will be always considered when not differently specified.



Figure 4.4: Transmittance spectra computed using the Transfer Matrix Method (TMM) for DBRs consisting of 10, 20 and 30 bilayers alternating PVK and CA layers with thicknesses of 80 nm and 90 nm respectively.

4.3.2 DBR optical response

The fabrication of a DBR is an iterative process finalized to the optimization of the physical (i.e. refractive index and absorbance of the processed materials) and geometrical (i.e. thickness of each layer of the DBR derived by fine tuning of solution concentration and spinning speed) parameters involved. The reproducibility of each step plays a key role in the optical characteristics of the final structure, hence it becomes essential to check the quality of the optical response of the DBR in order to ensure an excellent yield of fabrication for the whole microcavity structure.

In Figure 4.5 I report the measured transmittance spectrum of a 20-bilayer DBR composed by alternating layers of PVK and CA overlapped to the best fitting DBR structure calculated by TMM. The TMM model was found to fit the experimental data for layer thicknesses of 77 nm for PVK and 100 nm for CA with an excellent agreement with profilometric measurements carried out during the DBR fabrication giving thicknesses as of 77 ± 6 nm and

 95 ± 5 nm for PVK and CA respectively obtained over more than thirty thickness measurements. The slight variation from nominal values of layer thicknesses as reported in Section 4.3.1 determines a ~20 nm red shift in the optical response of the DBR centred at ~550 nm in Figure 4.5 whose spectral position results significantly sensitive to inhomogeneity.

Nevertheless, the agreement in the position of secondary peaks between the measured spectrum and the calculated one is notable and the small deviation of measured secondary peaks depth can be ascribed to the scattering of the surface which is not considered in the model and to the resolution of the spectrophotometer. However, the extended pattern of interference fringes is symptomatic of the structure quality and demonstrates the reliability of spin coating method assessed also by the overlap of the two spectra.



Figure 4.5: Measured transmittance spectrum of a 20-bilayer DBR compared to TMM calculated spectrum. The TMM model was built with layer thicknesses of 77 and 100 nm for PVK and CA respectively, while the thickness of the layers for the DBR measured by profilometry were 77 ± 6 nm and 95 ± 5 nm for PVK and CA respectively. Transmittance measurements have been carried out in air illuminating the sample at normal incidence with a halogen lamp and recording the spectrum in the same direction by using an Avantes spectrophotometer.

4.3.3 Microcavity characterization

4.3.3.1 Normal incidence transmittance and photoluminescence

In Figure 4.6 I report the transmittance spectrum of a microcavity composed by two DBRs of 25 PVK:CA bilayer incorporating an active layer of PDPV at 0° incidence angle. The thickness of PVK, CA and PDPV is about 80, 90 and 180 nm, respectively, having designed the thickness of the active layer equal to $\lambda_{cav}/2$, where λ_{cav} is the cavity mode wavelength. The microcavity exhibits a photonic stop-band in the range 490-580 nm (FWHM of the transmittance spectrum in Figure 4.6) which lies away from the absorption spectrum of PDPV peaking at 355 nm as shown in Figure 2.2 but has an excellent overlap the PL spectrum of PDPV which peaks at ~520 nm and is asymmetric with the respect to its peak with a lower-energy side which is twice more extended than the higher-energy side. The insertion of the defect PDPV layer induces the creation of a relative maximum in the transmittance spectrum which is located at ~535 nm and whose depth is limited by the spectrophotometer resolution. However, the complex pattern of interference fringes both sides of the stop-band shows a good uniformity of the thickness layers across the whole structure and at wavelengths lower than 400 nm the transmittance is decreased by the simultaneous influence of the absorption spectrum of PDPV.

The microcavity optical response strongly affects the fluorescence of the active layer of PDPV as shown in solid blue line in Figure 4.4 at 0° collection angle. The typical large emission band of PDPV which covers the full spectral range going from ~450 nm to ~700 nm is completely reshaped into an extremely narrow peak at ~540 nm where the photons squeeze and almost entirely suppressed in the spectral region where the stop-band insists. The interference fringes visible in the transmittance spectrum are reflected into the modulated emission spectrum outside of the stop-band. The microcavity provides the directionality to the emission of PDPV which is maximized at 0° collection angle, hence the quality factor, $Q = \lambda_c / \Delta \lambda_c$, can be derived by the PL spectrum in Figure 4.6 and equals 85 having measuring a FWHM of the PL spectrum of ~6.5 nm.



Figure 4.6: Measured normal transmittance (black) overlapped with the PL intensity (blue) at 0° collection angle of a microcavity composed by two DBRs of 25 bilayers of PVK:CA in between of which a PDPV layer of ~180 nm has been spin cast. Transmittance measurements have been carried out by using a halogen lamp hitting the sample and collecting the light with an Avantes spectrophotometer located along the same direction of the source. For PL measurements in air an excitation *ps*-pulsed laser emitting at 375 nm has been used and light has been collected at 0° by using an Andor spectrophotometer.

4.3.3.2 Enhancement of photoluminescence

Figure 4.7 compares the PL intensity of the microcavity made of two 25-bilayer DBRs incorporating the active PDPV measured at 0° collection angle with the PL intensity of a reference sample consisting of a PDPV layer in between of two PVK:CA bilayers. For the fabrication of the reference layer the same deposition parameters have been used in order to obtain a structure that resembles for PDPV the same environment it sees into the microcavity, i.e. the same interface with a CA layer, but not affected by the photonic response of the microcavity itself. As the measurements have been taken using the same condition exciting the samples at 375 nm a direct comparison of the two spectra in Figure 4.7 assess a notable 13-fold directional enhancement of the PDPV PL at 0° collection angle, while the PL linewidth shrinks to 6.5 nm which is ~18 times narrower than the FWHM measured for the reference sample. Both the PL enhancement and

linewidth sharpening are the highest reported so far at the best of my knowledge for all-polymer microcavities.



Figure 4.7: PL spectra at 0° collection angle with respect to the detector of a microcavity (blue) composed by two DBRs of 25 bilayers of PVK:CA with a PDPV layer of ~180 nm as defect layer placed in the middle of the cavity and of a reference sample in which the same PDPV layer is sandwiched in between of two PVK:CA bilayers fabricated using the same parameter reported in Experimental methods. Inset: Schematics of the reference sample (red squared) and microcavity sample (blue squared). PL measurements have been carried out in air using an angle-resolved PL setup exciting the samples at 375 nm and collecting the light at 0° by using an Andor spectrophotometer.

4.3.3.3 Angle-resolved transmittance and photoluminescence

The stop-band position of the microcavity is angularly dispersive with the angle of the incidence light, in fact the same trend can be measured for the cavity mode. Taking as reference the position of the cavity mode at normal incidence, its angular dispersion can be approximately predicted by using the Bragg-Snell law^[18] for higher diffraction orders (*m*) as per below

$$m\lambda_{cav} = 2d\sqrt{n_{eff}^2 - (\sin\theta)^2}$$
(4.2)

where λ_{cav} is the cavity mode wavelength, d the bilayer thickness, n_{eff} the effective refractive index of the structure and θ the angle of the incidence light. The effective refractive index is calculated considering refractive indices n_{PVK} and n_{CA} and thicknesses d_{PVK} and d_{CA} of PVK and CA (with the bilayer thickness $d = d_{PVK} + d_{CA}$)

$$n_{eff} = \frac{n_{PVK}d_{PVK} + n_{CA}d_{CA}}{d_{PVK} + d_{CA}}$$
(4.3)

Figure 4.8 reports the calculated dispersion of the cavity mode white-dashed in the bottom panel as function of the incidence angle obtained by using the Bragg-Snell equation overlapped to the contour plot of measured transmittance spectra of the microcavity for the same incidence angles. As expected by Eq. 4.2 the stop-band blue-shifts for increasing incidence angles and the measured (white crosses in Figure 4.8) and calculated spectral positions of the cavity defect fit well. Being the stop-band dispersive, the enhanced PL peak shifts towards lower wavelengths increasing the collection angle analogously.

The top panel of Figure 4.8 shows the PL spectra of PDPV in the microcavity for four collection angles between 0° and 45° with respect to the detector in 15° steps with the PL enhanced peak blue-shifting in the same way as the cavity mode in transmittance. As the PL intensity at higher angles is reported normalized to its maximum value at 0° it appears that the PL intensity is decreasing at larger collection angles, however these spectra demonstrate that the PL reshaping in the microcavity is unambiguously related to the photonic structure. Nevertheless, for angles larger than 50° here not reported the PL is not affected by the stop-band of the microcavity and is unchanged compared to the PL of the reference sample.



Figure 4.8: Top panel – PL intensity measured from the microcavity for four collection angles from 0° to 45° with respect to the detector in 15° steps. PL measurements have been carried out in air exciting the sample with a *ps*-pulsed diode laser emitting at 375 nm and changing the collection angle of the detector accordingly. Bottom panel – Contour plot of measured transmittance spectra of the microcavity as function of the angle of the incidence beam. White crosses identify measured transmittance spectra peaks wavelengths and are compared to calculated minima of the microcavity stop-band (white dashes) as derived by Bragg-Snell law. PL peaks in the top panel agree perfectly with the position of the relative maxima in transmittance spectra within the stop-band due to the presence of the defect layer. Transmittance measurements have been carried out in air by using a halogen lamp and an Avantes spectrophotometer in the same direction while turning the sample.

Regarding the PL enhancement effects, at 0° collection angle comparison between the microcavity and the reference PL spectra has been shown in Figure 4.7. The contour plot in Figure 4.9 reports the PL enhancement factor, EF_{PL} , given by the ratio of the microcavity-reshaped PL and the PL of the reference measured at the collection angles between 0° and 50°. The PL enhanced peak moves towards lower wavelengths as the collection angle is increased and its

dispersion fits perfectly the Bragg-Snell calculated trend (dashed black line in Figure 4.9). When the EF_{PL} is higher than one a PL enhancement is measured while where the stop-band insists spectrally the EF_{PL} tends to zero as the PL of the microcavity is almost completely suppressed.



Figure 4.9: Measured PL enhancement factor, $EF_{PL} = PL_{cav} / PL_{ref}$, as function of the collection angle and compared to calculated angular dispersion of the PL peak by Bragg-Snell law. PL measurements have been carried out in air exciting the samples (both the microcavity and the reference) with a *ps*-pulsed diode laser emitting at 375 nm and changing the collection angle of the detector accordingly.

4.3.3.4 Photoluminescence quantum efficiency and lifetime decays

A crucial characteristic of microcavities is given by the possibility of modifying the radiative emission rate of the incorporated emitter as described in Section 1.4.1. As the radiative rate represents the number of emitted photons per unit time in the absence of non-radiative processes, a higher rate can be useful for more efficient lighting and for optical fibre communication. The variation of the photonic density of states (*PDOS*) demonstrated by the reshaping of the PL in the microcavity affects the radiative rates as per Eq. (1.4). Also, the simplified relations shown in Eq. (2.2) relate easily the effective radiative, k_R , and non-radiative, k_{NR} , rates to PL quantum yield (PL QY, η) and PL lifetime, $\langle \tau \rangle$, therefore a variation of k_R and

 k_{NR} in the microcavity with respect to the reference sample can be assessed by experimental measurements of PL efficiencies and PL temporal decays.

Indeed, I measured an increase by ~8 \pm 2 % in PL QY in the microcavity (55 \pm 2 %) compared to the reference sample (51 \pm 2 %) by using an integrating sphere and following the method reported by de Mello^[107], having excited both the samples at 375 nm and measured the PL QY over the whole spectrum. The PL QY of the PDPV reference sample is the same as reported in Section 2.3.1 and 3.3.1 despite the different environment which surrounds the PDPV layer which is completely encapsulated by two PVK:CA bilayers which prevent any effect of photo-bleaching and photo-oxidation.

Once assessed the PL QY increase of PDPV in the microcavity compared to neat PDPV, to gain further insight into the underlying photophysics of all-polymer microcavities, I carried out time-resolved PL measurements at the cavity mode wavelength and both in the low- and high-side of the photonic stop-band of the microcavity. First, PL spectra of the reference and the microcavity have been measured in air and at room temperature exciting the samples at 375 nm which were positioned at 20° collection angle with respect to the detector. In Figure 4.11, normalized PL spectra are shown in the top panels. While the PL emission of PDPV in the reference sample is unchanged compared to the one reported in Figure 2.2 peaking at ~520 nm, the microcavity emission is strongly modulated by the photonic structure enhanced at $\lambda_{cav} = 525$ nm and suppressed in correspondence to the stop-band edges, i.e. at $\lambda_{sbh} = 515$ nm for the stop-band high energy side and at $\lambda_{sbl} = 540$ nm for the stop-band low energy side, similarly to what has been described in Figure 4.7.

However, a 15-nm blue-shift in the position of the cavity mode is measured in the PL spectrum of the cavity when measured with the TCSPC. The cavity mode is located at 540 nm in Figure 4.7, but the blue shift here reported is due to the fixed collection angle of the detector in the PL lifetime setup. Figure 4.10 shows a top view of the TCSPC chamber used for the lifetime measurements. The laser pumping the sample is normally incident to the microcavity which is rotated by 20° with respect to the detector. The measured blue-shift agrees perfectly with the expected blue-shift shown in Figure 4.8 for a collection angle of 20°.



Figure 4.10: Image of the TCSPC chamber used for PL steady-state and lifetime measurements. The laser is normally incident to the sample which is rotated by 20° with respect to the detector.

In the lower panels of Figure 4.11, I report the lifetime decay maps of the same samples mirrored with respect to 620 nm. At 620 nm the decays have the same temporal extension not being subjected to any variation due to the photonic structure. For the reference sample the PL lifetime is constantly extending as it is detected at larger wavelengths due to the bigger contribution to PL of aggregated species which is characterized by a longer lifetime. On the other side, the PL lifetime of PDPV in the microcavity is notably modulated by the modification of the PL due to the photonic structure. The cavity mode and stop-band wavelengths where PL lifetimes have been measured are highlighted in Figure 4.11. The lifetime extension is shortened at $\lambda_{cav} = 525$ nm where the cavity mode is spectrally located and clearly extended in the stop-band with a longer lifetime in the low-energy side ($\lambda_{sbl} = 540$ nm) than in the higher-energy side of the spectrum ($\lambda_{sbh} = 515$ nm) where the aggregated state contribution to fluorescence is lower. The residual modulation of lifetime due to secondary interference fringes of the microcavity does not affect the PL lifetime significantly.



Figure 4.11: Top panels: Normalized PL spectra of PDPV in the reference (left) and in the microcavity (right) between 450 nm and 620 nm. Bottom panels: Lifetime decay maps of the reference and the microcavity as function of the emission wavelength between 450 nm and 620 nm. Insets: Schemes of reference and microcavity structures. All measurement were taken in air and at room temperature positioning the samples with a collection angle of ~20° with respect to the detector and exciting the samples by a *ps*-pulsed laser emitting at 375 nm.

Figure 4.12 shows the detailed temporal evolutions of PDPV in the reference sample (black lines) and in the microcavity (red lines) compared (a) at $\lambda_{sbh} = 515$ nm (high-energy side of the stop-band), (b) in the cavity mode $\lambda_{cav} = 525$ nm (in the cavity mode) and (c) at $\lambda_{sbl} = 540$ nm (low-energy side of the stop-band). At $\lambda_{sbh} = 515$ nm (a) and at $\lambda_{sbl} = 540$ nm (c), where a

suppression of PL ($EF_{PL} < 1$) has been measured, the decay for the reference sample is shorter than for the microcavity, while in the cavity mode $\lambda_{cav} = 525$ nm (b), where the PDPV PL is enhanced ($EF_{PL} > 1$), the decay of PDPV in the microcavity is clearly shorter than the one in the reference sample.

PL dynamics in Figure 4.12 have been fitted by a bi-exponential expression, $I(t) = A + B_1 e^{-\frac{t}{\tau_1}} + B_2 e^{-\frac{t}{\tau_2}}$ as already described for solid-state films in Section 3.3.2. PL lifetimes, τ_1 and τ_2 , and relative contribution to PL decays of each species, I_1 and I_2 , calculated as per Eq. (2.1) are reported in Table 6. The fitted values for the two lifetimes in the reference and in the microcavity are generally shorter than the lifetimes measured for neat PDPV, however the environment surrounding the PDPV layers due their encapsulation in between of cellulose acetate layers determines this variation. Furthermore, the relative contribution of the emissive species are almost constant despite of the structure and emission wavelength tested with a predominance of the aggregate contribution to the total PL of PDPV. These data are in full agreement with those reported for PDPV:PVK blends in Section 3.3.2.

Looking at the lifetime values, τ_l and τ_2 , as expected by the lifetime plots in Figure 4.12, within the cavity mode (b) the exciton lifetime τ_l is reduced by ~11% (0.93 ns in the microcavity vs. 1.05 ns in the reference) while the aggregated state is affected less by the photonic structure with a decrease of about 4%, hence the average reduction in the cavity mode is by 7% with respect to the reference. On the other hand, the trend seems symmetrical for PL lifetimes in the stop band (a) and (c), where both the lifetimes are longer in the microcavity than in the reference sample in agreement with the expected reduced availability of photonic states in the two edges of the cavity mode. The average effect on lifetime is the increase of the lifetime by ~4.5% at $\lambda_{sbh} = 515$ nm (a) (high-energy side of the stop-band) and by ~9.7% at $\lambda_{sbl} = 540$ nm (c) (low-energy side of the stop-band). I attribute the latter slight difference to a stronger effect of the photonic structure at higher wavelengths where the microcavity transmittance is null as shown in Figure 4.6.



Figure 4.12: Temporal evolution of PDPV in the reference (black lines) and in the microcavity (red lines) measured (a) at $\lambda_{sbh} = 515$ nm (high-energy side of the stop-band), (b) at $\lambda_{cav} = 525$ nm (in the cavity mode) and (c) at $\lambda_{sbl} = 540$ nm (low-energy side of the stop-band). All measurement were taken in air and at room temperature positioning the samples with a collection angle of ~20° with respect to the detector and exciting the samples by a ps- pulsed laser emitting at 375 nm.

Wavelength (nm)	τ_1 , ns (I ₁)	τ_2 , ns (I ₂)	<\alpha>, ns
515 nm (high-energy side stop-band)			
Reference	1.03 ± 0.04	3.05 ± 0.06	2.43 ± 0.10
	(0.31)	(0.69)	
Microcavity	1.08 ± 0.05	3.12 ± 0.06	2.54 ± 0.10
	(0.28)	(0.72)	
525 nm (cavity mode)			
Reference	1.05 ± 0.05	3.07 ± 0.06	2.54 ± 0.11
	(0.26)	(0.74)	
Microcavity	0.93 ± 0.04	2.93 ± 0.05	2.36 ± 0.09
	(0.29)	(0.71)	
540 nm (low-energy side stop-band)			
Reference	1.33 ± 0.06	3.49 ± 0.10	2.78 ± 0.16
	(0.33)	(0.67)	
Microcavity	1.59 ± 0.10	3.68 ± 0.13	3.05 ± 0.21
	(0.30)	(0.70)	

Table 6: Lifetime values, τ_1 and τ_2 , with relative contribution to PL of each species in brackets and average lifetime, $\langle \tau \rangle$, of PDPV in the reference structure and in the microcavity derived by the fit of PL decays in Figure 4.12. The χ^2 value on all the fits is included between 1.0 and 1.1.

Using Eq. (2.2), I obtained the effective radiative, k_R , and non-radiative, k_{NR} , decay rates shown in Table 7. The small variation of average lifetimes in the edges of the stop-band results in small changes in k_R and k_{NR} within the error bar of each value. Nevertheless, at the cavity mode while k_{NR} is unchanged within the two structures, an increase of the radiative rate k_R by 16.5% is derived and for the first time reported at the best of my knowledge for all-polymer microcavities assessing their viability for more efficient communication rate, despite the large mode volume of a planar microcavity distributed over the whole microcavity surface. From the physical point of view, the variation in the radiative lifetime allows the measurement of a sizeable Purcell effect, which represents the enhancement of the spontaneous emission rate of a system caused by its environment. In this case, PDPV is changing its radiative rate when incorporated in a resonant microcavity.

Wavelength (nm)	$k_R (10^8 \text{ s}^{-1})$	$k_{NR} (10^8 \text{ s}^{-1})$
515 nm (high-energy side stop-band)		
Reference	2.10 ± 0.12	2.01 ± 0.16
Microcavity	2.16 ± 0.12	1.77 ± 0.13

 2.00 ± 0.12

 2.33 ± 0.12

 1.84 ± 0.13

 1.80 ± 0.14

 1.93 ± 0.15

 1.91 ± 0.14

 1.76 ± 0.16

 1.47 ± 0.14

Table 7: Radiative, k_R , and non-radiative, k_{NR} , effective rates for PDPV in the reference structure and in the microcavity at the cavity mode, calculated as per the model proposed in the text.

4.4 Conclusions

Reference

Microcavity

Reference

Microcavity

540 nm (low-energy side stop-band)

In conclusion, I reported on all-polymer microcavities doped with PDPV through a lowcost fabrication process based on spin coating. The photoluminescence of PDPV in microcavities with quality factor of about 85 exhibits an enhancement by ~13 times at the cavity mode and a reduction of ~18 times for the PL full width at half maximum while it is suppressed at the edges of the cavity mode. The PL spectra are dependent on the collection angle and the enhancement of PL has been measured up to 50°. Simultaneously, the PL average lifetime has decreased by 7% in the cavity mode and increased in the stop band (~9% at longer wavelengths). The decrease of the PL average lifetime at the cavity mode has induced an increase in the radiative rate by 15.6% and this effect can be ascribed to the variation of the photonic density of states. In the future, the sizeable Purcell effect here reported may be enhanced by either improving the quality of the microcavity (e.g. increasing the index contrast of constituting materials) or reducing the volume mode by means of quantum walls and dots where the active material is located.

5 All-polymer microcavities doped with nearinfrared emitters

5.1 Introduction

A plethora of applications spanning from photodynamic therapy^[139] to security and defence^[140] have increased the attention of researchers towards near-infrared (NIR) emitters in the last decade. Furthermore, NIR radiation is defined for wavelengths included in the range 700-1000 nm and is mostly invisible to the human eye, hence NIR light-emitting sources are outstanding candidates for the development of Li-Fi (Light-Fidelity) all-optical networking systems, which can help in overcoming the limitations of bandwidth affecting wireless (Wi-Fi) systems.^[141]

Organic NIR emitters provide an unlimited range of designs and configurations able to fit the requirements of any application, thanks to their mechanical flexibility and biocompatibility. However, the implementation of NIR emitters into organic light-emitting diodes (OLEDs) or other lighting sources presents some challenges due to physical limitations of such materials. In order for a conjugated material to emit in the NIR range, an extended conjugation length is essential but it is dependent on a very planar molecular conformation of the polymer which determines the formation of photoluminescence-quenching players such as *H*- aggregates^[142] and can be tackled by different strategies, such as dilution of chromophores in solid-state matrices^[17, 47-49] or molecular design^[50-52]. Another hurdle to be considered is the socalled "energy-gap" law which predicts the non-radiative transitions increases exponentially for materials with lower energy-gaps.^[143] In fact, NIR emitters are featured by generally low photoluminescence efficiencies.

Recently, NIR emitters incorporating heavy elements which are often toxic have been reported as active layers in NIR OLEDs with external quantum efficiencies (*EQEs*) around 10% or over^[144]. However, the research of "heavy-metal-free" NIR emitters is a crucial point for future developments in the field and conjugated porphyrins oligomers are excellent candidates.

5.2 Conjugated porphyrin oligomers

Conjugated porphyrin oligomers are an intriguing class of NIR emitters, exhibiting extraordinary electro-optical and nonlinear optical properties, and have been synthesised by a very few groups in the world, including the group of Prof. Harry L. Anderson at the University of Oxford, UK^[145, 146] and the group of Prof. Michael J. Thérien at the University of Durham, North Carolina, US^[147, 148]. Their use has been proposed in a wide range of applications, spanning from artificial photosynthesis^[149] and photodynamic therapy^[150] to novel materials for linear and non-linear optical applications^[151, 152]. For the latter, the optical properties of porphyrins can be tuned by substitution of the central atom of the ring with different metals or by grafting various electroactive groups in the peripheral positions of the ring. Furthermore, the optical properties of porphyrins oligomers can be tuned from the visible range to the near-infrared range (<1000 nm) by extending significantly the conjugation length across the entire molecule connecting the porphyrins via *meso-ethyne*^[153, 154] or *meso-butadiyne*^[17, 146] links.

The extended conjugation length of porphyrin oligomers induce strong electronic transitions and very intense absorption bands in the visible and near infrared (NIR) range.^[152] Two transitions are present since the monomeric structure: the first from the ground state to the second excited state ($S_0 \rightarrow S_2$) peaking in the region around 450 nm that is strong and defines the so-called Soret or *B*-band and the second from the ground to the first excited state ($S_0 \rightarrow S_1$) that determines the *Q* band and is weaker in the monomer but becomes stronger and red-shifts as the number of repeating units of porphyrins increases.^[145] Polarized spectroscopy also reveals that each of *B* and *Q* bands exhibit a low-energy side (B_x and Q_x respectively) polarized in the axis along which the porphyrin units are joined in an oligomer, whereas the high-energy components, B_y and Q_y , are polarized in the direction perpendicular to the B_x and Q_x , in the plane of porphyrin rings.

Furthermore, fluorescence takes place only from S_1 as the internal conversion from S_2 to S_1 happens in *ns*-regime. As known for all NIR emitters, the extended π -conjugation is essential to obtain NIR emission, but the photoluminescence quantum yield decreases for NIR emitters due

to the increase of the vibrational overlap between excited and ground states. For this reason, novel design approaches for porphyrin oligomers to improve NIR-OLEDs efficiencies and avoid the aggregation of the species (with the use of pyridine) in the solid state have been reported in the literature by Fenwick *et al.*,^[17] where high photoluminescence quantum yield as of 7.7% was measured. On the other hand, more complex structures, such as porphyrin nanorings^[155], can be advantageous to prevent quenching of the photoluminescence for photonic applications.

However, the extended and delocalised π -electron system suggests the presence of very high cubic nonlinear susceptibility^[156]. Porphyrins and phtalocyanines, based on macrocycles, represent excellent materials for optical limiting^[157] and switching^[158], due to the sharp absorption transitions and stability under large optical irradiation for all-optical switching. In addition, the interest for near infrared spectral range of telecommunications makes porphyrins particularly attractive for devices where porphyrins can be adopted as switching materials. Indeed, porphyrins have been measured by many spectroscopic techniques, such as optical absorption^[151], quadratic electroabsorption^[156], polarised electronic absorption^[145], field-induced absorption^[159], femtosecond transient absorption^[160] to investigate their potentiality for optoelectronic and photonic applications.

Here, I will report the optical, electrical and morphological characterization of a novel series of trihexylsylil (*THS*) grafted zinc porphyrin oligomers, *l-Pn(THS*), whose monomer is shown in Figure 5.1, where *n* is the number of monomeric units. They possess diacetylenic bridges between the macrocycles, which allow the extension of the π -conjugation enabling NIR emission and boost the radiative rate increasing the mismatch of singlet and triplet excitons spatial extent. In addition long side chains (*THS*) were introduced in the molecule design to prevent aggregation quenching more effectively than in a previously reported linear hexamer^[17], thanks to steric hindrance by the *THS* groups, which limits π - π interactions.

5.2.1 Experimental methods

Films preparation. The conjugated zinc porphyrins presented here and shown in Figure 5.1 were synthesised at the University of Oxford in the group of Prof. H. L. Anderson. Details of the synthesis can be found in Ref. [161]. Several samples have been used in the experiments for increasing number of monomeric units, such as l-Pn(THS) where n = 2, 4, 6, 8, N. l-PN(THS) is the longest porphyrin oligomer with a wider distribution of monomeric units centred at 12 but with chains between 8 and 20 units. Porphyrin oligomers were dissolved into toluene solutions concentrated at 10 mg/ml and spin-cast onto fused silica substrates in an inert N_2 environment at 1500 rpm for 90 seconds to obtain ~80 nm thick films. To investigate the influence of a thermal annealing on l-Pn(THS) on optical and morphological characteristics, different samples of porphyrin films have been annealed at 50, 100, 150 °C for 10 minutes in N_2 environment.



Figure 5.1: Chemical structure of the *l-Pn(THS)* oligomers.

TFT preparation. Thin film transistors (TFTs) have been fabricated to test the electrical characteristics of l-Pn(THS) oligomers. I purchased TFT substrates from Fraunfhofer IPMS, Dresden, Germany. The basic bottom-gate structure used in this experiment is sketched in Figure 5.2. The basic TFT is composed by two ohmic interdigitated contacts (source and drain) consisting of a 10 nm thick ITO layer and 30 nm thick gold layer. Their distance is the channel

length of the TFT and on a substrate four TFTs for each channel length (20, 10, 5 and 2.5 μ m) are present. The gate contact is an *n*-doped (3 · 10¹⁷ cm⁻³) silicon wafer and the gate dielectric is a 230 nm thick silicon dioxide, thermally grown.

The substrates were washed in 10 minutes ultrasonic baths of both acetone and 2-propanol (IPA) at room temperature and treated by oxygen plasma. The porphyrin oligomer layer was spin cast at 1500 rpm for 90 s after the deposition of a self-assembled monolayer such as *hexamethyldisilazane* (HMDS, spin cast on the sample, annealed at 100°C and spin-washed with propan-2-ol) which improved the self-organisation of the conjugated oligomer/polymer at the interface with the dielectric. To investigate the influence of a thermal annealing on *l-Pn(THS)* on electrical characteristics, different samples of porphyrin films have been annealed at 50, 100, 150 °C for 10 minutes in N_2 environment.



Figure 5.2: Transistor substrate on the right containing 16 transistors, 4 for each channel length (20, 10, 5 and 2.5 μ m). On the left details of the layer stack of the device fabricated on an *n*-doped (3·10¹⁷ cm⁻³) silicon wafer with 220 nm-thick silicon dioxide thermally grown on top. Contacts are made of 10 nm-thick indium tin oxide (ITO) layer and 30 nm-thick gold (Au) layer and *l-Pn(THS)* have been spin-cast on top.

Characterization methods. Optical absorption spectra have been measured using an Agilent 8453 UV-Vis spectrophotometer. Transfer and output characteristics of transistors have been measured using a Karl Suss PM5 probe station (inside a nitrogen glove box) and an HP4145 parameter analyser. Surface morphology has been investigated by using atomic force microscopy (AFM, Dimension Icon). All AFM images were recorded using tapping mode in air.

5.2.2 Porphyrin oligomers characterization

5.2.2.1 Absorption spectra

Figure 5.3 shows the UV-Vis-NIR absorption spectra of films of *l-Pn(THS)* for different chain lengths (n = 2, 4, 6, 8, N) at room temperature. Reflection is not corrected. Each spectrum presents a couple of strong macrocycle-derived π - π * absorption bands: a high-energy band (Soret or *B*-band) and a low-energy band *Q*-band.

The *B*-band is spectrally constant as a function of the increasing chain lengths and its shape is determined by two perpendicular components, B_x and B_y , of the transition dipole which splits the excited state. In *l*-*Pn*(*THS*), B_x lays down the direction of the chain (head-to-tail) and has lower energy^[145], thus its contribution to the absorption is the low-energy side of the *B*-band whose strength increases as the chain is extended. B_y is in the plane of the chain but normal to B_x and is related to the high-energy side of the *B*-band. Furthermore, B_x is unaffected by possible torsions of the chain in the solid state and its peak is sharp, while B_y is broader and less strong as much as its transition dipole decreases when two close porphyrin units are tilted one with respect to the other because of decreasing dipoles coupling.

The *Q*-band is affected by stronger changes in its low-energy part (Q_x), while the highenergy Q_y band is fairly constant in its spectral position especially for n > 6. The extended delocalisation of the π -electron system implicates an extremely pronounced red-shift of the lowest energy transition (Q_x) and a significant increase in the dipole strength going from the dimer, which peaks at 693 nm, to the polymer, whose absorption peak is located at 816 nm. According to Kasha's theory, these features are typical for *J*-aggregates which exhibit also narrow absorption bands, as shown here for longer oligomers.



Figure 5.3: Absorption spectra of *l*-*Pn*(*THS*) oligomers spin cast on fused silica substrates for n = 2, 4, 6, 8, N between 300 nm and 1000 nm measured in air at room temperature.

The absorption spectra of *l*-*Pn*(*THS*) oligomers for n = 4, 6, 8, N, thermally annealed at $T_A = 50$, 100, 150 °C or left untreated at room temperature (R.T.) have been measured and reported in Figure 5.4. The *l*-*P2*(*THS*) absorption spectra are not shown as function of the annealing temperature as no change has been recorded. The *Q*-band wavelength peak of *l*-*P4*(*THS*) absorption spectra show an increasing number of peaks and a total blue-shift of ~50 nm for increasing T_A , whereas for longer oligomers the *Q*-band absorption peak does not move but the FWHM is progressively more narrow.

Generally speaking, the *B*-band for each oligomer does not move spectrally for different chain lengths nor as function of the annealing temperature, while the *Q*-band is significantly affected by the thermal treatment which induces a certain degree of crystallinity. Indeed, for higher temperatures for all oligomers more resolved peaks appear in the absorption spectra and correspond to optical transitions for different conformers, which behave as distinct species. In solution porphyrin oligomers are freer to rotate than in solid state and the *Q*-band is featureless for all the oligomers except the dimer which exhibits two distinct species. The main component of the *Q*-band in solution is the planar conformer which has the highest oscillator strength.^[162] In

solid state the disorder is reduced and some conformers created by torsions of porphyrins along the chains are predominant, hence in the *Q*-band of the absorption spectra of films the vibronic transitions associated to these conformers prevail.



Figure 5.4: Absorption spectra of *l-Pn(THS)* oligomers spin cast on fused silica substrates for n = 4, 6, 8, N between 300 nm and 1100 nm measured in air at room temperature. One sample for each oligomer length was left untreated after deposition at room temperature (R.T.) while three samples were annealed for 10 minutes in N_2 environment at $T_A = 50, 100, 150 \text{ °C}$.

5.2.2.2 Electrical characterization

In organic semiconductors, charges origin localised states within the electronic bandgap. Between these states, transport occurs by hopping of charges. The mobility of a charge carrier is expressed by the ratio between the drift velocity, v_d , and the electric field, E, and is quite low at room temperature and strongly dependent on the morphology.^[7] For disordered films typical values of mobility are included between 10^{-6} and 10^{-2} cm²V⁻¹s⁻¹.

Organic TFTs allow to measure the carrier mobility in an organic semiconductor. They usually operate in accumulation mode, which means for *p*-channel transistors that holes are located in the semiconductor near the SiO₂ layer shown in Figure 5.2 when a negative V_{GS} is applied. The drain current, I_D , can be modulated by varying the input gate-source voltage V_{GS} . This dependence is described by the transconductance g_m as follows

$$\mathbf{g}_{\mathrm{m}} = \frac{\partial \mathbf{I}_{\mathrm{DS}}}{\partial \mathbf{V}_{\mathrm{GS}}} | \mathbf{V}_{\mathrm{DS}} = \mathrm{const} \tag{5.1}$$

and measured by transfer characteristics. Eq. (5.1) determines μ (proportional to the slope of the curve) and V_{th} (by the square root of the transfer curve).

The I_D - V_{DS} output characteristics are described by the same model used for inorganic transistors and the equation in saturation, i.e. $|V_{DS}| > |V_{GS} - V_{th}|$ where V_{th} is the threshold voltage beyond which the drain current increases significantly, is

$$I_{DS,sat} = \frac{W}{2L} \mu C_i (V_{GS} - V_{th})^2$$
(5.2)

where *W* is the channel width, *L* is the channel length, μ is the carrier mobility, *C_i* is the gate dielectric capacitance per unit area. Figure 5.5 shows the output characteristics of *l-P6(THS)* thermally untreated for four channel length (20, 10, 5 and 2.5 μ m) measured by sweeping the drain-source voltage from 0 V to -80 V and from -80 V to 0 V for each fixed gate-source voltage. The hysteresis of the sample, i.e. the difference between drain current values obtained by positive and negative sweeps, is remarkably low.


Figure 5.5: Output characteristics of *l-P6(THS)* thermally untreated for four channel length (20, 10, 5 and 2.5 μ m) measured by sweeping the drain-source voltage from 0 V to -80 V and from -80 V to 0 V for each fixed gate-source voltage.

Main *l-Pn(THS)* parameters for thermally untreated TFTs have been extracted by the transfer characteristics and reported in Table 8. The ON/OFF ratio is the ratio between the drain current in saturation regime ($V_{DS} = V_{GS} = -80$ V here) and the drain current when the channel is not formed yet, i.e. a leakage current ($V_{DS} = -80$ V and $V_{GS} = 0$ V). It is fairly constant over the porphyrin oligomers length and has typical values with respect to OTFTs ($\sim 10^4 - 10^5$). Furthermore, threshold voltage is decreased and carrier mobility is increased as function of the chain length. In particular the carrier mobility rises three order of magnitude from the dimer to the polymer.

Oligomer	I_{ON}/I_{OFF}	$\mathbf{V}_{\mathbf{th}}\left(\mathbf{V} ight)$	μ (cm²/(Vs))
<i>l</i> -P2	$1.2 \cdot 10^4$	-18.8	3.7.10-9
<i>l</i> -P4	$1.3 \cdot 10^4$	-12.8	3.3.10-7
<i>l</i> -P6	1.6.104	-10.5	$1.9 \cdot 10^{-6}$
<i>l</i> -P8	$1.8 \cdot 10^4$	-8.7	3.9.10-6
<i>l</i> -PN	$2.4 \cdot 10^4$	-7.5	7.6.10-6

Table 8: ON/OFF ratio, threshold voltage, V_{th} , and carrier mobility, μ , of *l-Pn(THS)* for active films thermally untreated.

Finally, Figure 5.6 reports the carrier mobility values extracted by transfer characteristics of *l-Pn(THS)* transfer characteristics as function of the annealing temperature for all fabricated devices. The carrier mobility increases significantly as derived from *l-P2(THS)* to *l-PN(THS)* ($2 \cdot 10^3$ higher for devices post-annealed at 150 °C) and from untreated transistors to 150 °C-annealed transistors (~ twice higher for the polymer).



Figure 5.6: Carrier mobility of *l-Pn(THS)* for n = 2, 4, 6, 8, N as function of the annealing temperature. One sample for each oligomer length was left untreated after deposition at room temperature (R.T.) while three samples were annealed for 10 minutes in N_2 environment at $T_A = 50, 100, 150$ °C.

The mobility values are still low for the actual implementation of porphyrin oligomers into proper electronic circuits. However, their electrical characterization may help the interpretation of electrical devices such as OLEDs or OLETs where porphyrin oligomers may be embedded as NIR emitter.

5.2.2.3 Morphological characterization

In Figure 5.7 the height images of l-P2(THS), l-P4(THS), l-P6(THS), l-P8(THS) and *l- PN(THS)* measured by atomic force microscopy are shown for samples where no thermal treatment was applied (R.T.) or thermal annealing was carried out at 50, 100, 150 °C.

The differences between the various thermal treatments are more pronounced for *l*- *P4*(*THS*), *l*-*P6*(*THS*) and *l*-*P8*(*THS*) similarly to what found out for the optical characteristics. Where the vibronic structures were more resolved in the absorption spectra, the surface has higher roughness R_q and possible nanocrystalline domains appear. Besides, the morphology of *l*- *P2*(*THS*) is extremely different, the films are not homogeneous, small clusters seem to be not interconnected each other since the untreated sample, the roughness decreases with the annealing temperature and no change in the absorption have been noticed as previously discussed. Finally, for *l*-*PN*(*THS*) films the small variations in the absorption films result in little changes in the morphology due to the larger size of oligomers.

In any case, the porphyrin surface is extremely smooth for all l-Pn(THS) films except for the dimer and this is valuable for their application within electronic and photonic devices.



Figure 5.7: AFM height mages of *l-P2(THS)*, *l-P4(THS)*, *l-P6(THS)*, *l-P8(THS)* and *l-PN(THS)* without annealing and for $T_A = 50$, 100, 150 °C spin cast onto fused silica substrates. All images are on a 5x5 μ m² area.

5.3 NIR all-polymer microcavities

All-polymer microcavities can be potentially disruptive for their application in light management, photovoltaics and lasing, as already mentioned in Section 4.1. Here, I report the optical characterization of all-polymer flexible microcavities incorporating a conjugated porphyrin oligomer, namely *l-PN(THS)*, emitting at ~890 nm. The enhanced and spectrally sharp photoluminescence from optical microcavities in the near-infrared (NIR) region can enter in the spotlight for biological imaging and sensing applications.

5.3.1 Experimental methods

Films preparation. The conjugated porphyrin oligomer, *l-PN(THS)*, shown in Figure 5.1 and employed here as NIR emitter into all-polymer microcavities have been synthesised at the University of Oxford in the group of Prof. H. L. Anderson. Details of the synthesis can be found in Ref. [161]. *l-PN(THS)* was blended with a host polymer such as *poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)]*, namely F8BT, whose chemical structure is shown in Figure 5.11a, purchased by American Dye Source. Thin films were spin-casted onto fused silica substrates from a 10 mg/mL toluene solution of the F8BT:*l-PN(THS)* blends.

Fabrication of microcavities. *Polyvynilcarbazole* (PVK, Mw = 90,000) and cellulose acetate (CA, Mw = 61 000) has been used for multilayer growth as high refractive index material and low refractive index material, respectively. PVK was sourced from Acros Organics and CA was purchased from Sigma Aldrich and used without further purification. Toluene and diacetonalcohol (*4-hydroxy-4-methyl-2-penthanon*) were used to prepare polymer solutions with a concentration of 30 mg/ml for PVK and 30 mg/ml for CA. The deposition of PVK:CA DBRs was performed by spin-coating (Süss Microtech Lithograghy GmbH AK200169) over glass substrates in laboratory environment without temperature or humidity control. Only for PVK layers, a further annealing process of 60 s at 70 °C on a hot plate was added to ensure the layer was completely dry. Layer thickness was selected by changing the spinning speed and solution concentrations. The samples analysed in this work were made of 25 bilayers DBRs with nominal thicknesses 130 and 150 nm for PVK and CA layers, respectively, spin-cast at 3100 rpm and measured using a Dektak³ profilometer from Veeco Instruments. The microcavity was obtained by spinning a *l-PN(THS)*:F8BT toluene solution (30 mg/ml) over a multilayer made of 25 bilayers PVK-CA films at 4550 rpm. Then, an additional 25 CA-PVK bilayers were grown over the PDPV film to complete the structure. The nominal thicknesses employed in this experiment allow the overlap between the stop-band of the microcavity and the emission of the NIR oligomer embedded in the structure.

Optical characterization of porphyrins microcavities. Absorption spectra of PDPV were collected using an Agilent 8453 UV-Vis spectrometer. The complex refractive index, n+ik, was determined by spectroscopic ellipsometry with a variable angle spectroscopic ellipsometer (VASE) by J. A. Woollam Co. Inc. with incidence angles ranging from 55° to 65° and analysed using the commercial software WVASE32. I carried out ellipsometric measurements in the group of Prof. Maddalena Patrini at the University of Pavia. This powerful instrument is ideal to measure both the thickness and the optical constants of thin films in a broad spectral region from 193 nm to 2500 nm. The technique consists of the measurement of the change in the polarization of incident light beam reflected from the surface of the sample. The change in the polarization is expressed by the ratio of complex reflection Fresnel coefficients, r_p and r_s , which depend on the refractive index of the sample and the incidence and refraction angles of the incident beam. The optical constants are obtained indirectly from the ellipsometric measurements upon the modelling of the absorption spectrum of each layer of the structure, followed by the fitting of the ellipsometric measurements using Levenberg-Marquardt algorithm.

Sample uniformity and thickness check over large areas $(2x2 \text{ cm}^2)$ has been performed by illuminating the samples with an Ocean Optics halogen lamp normally to the surface of the structure while an Andor Technology EMCCD (SR1 631) spectrometer has been used to measure the transmittance spectra. Angle-resolved transmittance spectra for both *S*- and *P*-polarizations were measured with the same setup above positioning the samples on a mobile goniometer and turning the sample at 5° steps. Angle-resolved PL spectra were collected with a setup consisting of an excitation source such as CW diode laser (Thorlabs, $\lambda_{exc} = 405$ nm) hitting on the sample at a fixed angle of 10° from the sample plane and an Andor Technology EMCCD (SR1 631) spectrometer placed normal to the sample and then moved with increments of 5° , such that only photons from PL directional contributions at variable collection angles are measured, keeping off the reflection of the laser. PL efficiency has been measured by means of an integrating sphere exciting the samples at 405 nm following the method described in [107]. Time-resolved PL measurements were carried out by Dr. Giuseppe Maria Paternò and Dr. Egle Molotokaite at Italian Institute of Technology, Milan, using a femtosecond laser source Ti:Sapphire laser (Coherent Chamaleon Ultra II, pulse bandwidth ~ 100 fs, repetition rate of 80 MHz, and power < 1 nW), useful to pump a second-harmonic crystal (barium borate) and tune the pump wavelength to 400 nm, coupled to a single photon detector sensitive in the NIR region. The angle of the incidence laser was kept fixed at 45° and the collection angle at 0° to avoid photonic dispersion. Measurements were carried out as function of the source fluency and decreasing the slit aperture to improve spectral resolution.

5.3.2 Optical characterization

5.3.2.1 *l-PN(THS) films*

Figure 5.8 shows the absorption and PL spectra of *l-PN(THS)*, which is the longest oligomer of the linear zinc porphyrin class characterized in Section 5.2.2. The main spectral components in the absorption spectrum are the high-energy or *B*-band due to the second-excited state (S_0 - S_2) and spectrally located between 400 and 550 nm and the low-energy or *Q*-band (S_0 - S_1) peaking at 825 nm. The fluorescence arises from S_1 exhibiting its maximum at 854 nm and a narrow full width at half maximum of ~83 nm.

The conjugation length of *l-PN(THS)*, which is more extended than the shorter oligomers shown in Section 5.2.2 affects its optical properties red-shifting the absorption spectrum, narrowing the emission band and reducing the Stokes' shift. All these features are very typical for *J*-aggregates that *l-PN(THS)* resemble for its linear *meso-butadiyne*-linked chemical structure. However, the PL quantum efficiency of pure *l-PN(THS)* in solid state is still low (<1 %) despite of the *THS* side chains designed to prevent aggregation.



Figure 5.8: Absorption and photoluminescence spectra of *l-PN(THS)*, whose chemical structure has been reported in Figure 5.1, spin-cast on fused silica substrate and measured at room temperature. The sample has been excited by a CW diode laser emitting at 405 nm.

The determination of the complex refractive index of l-PN(THS) is a delicate step for the design of the microcavity. After measuring the absorption spectrum of l-PN(THS) shown in Figure 5.8, the sample has been modelled by a Sellmeier transparent dispersion for the fused silica substrate and a new model including eight Lorentzian oscillators for l-PN(THS) located, in first instance, at the resonant frequencies of the absorption spectrum in Figure 5.8. Absorbance and ellipsometric spectra at different incidence angle of the light have been fitted together minimizing the mean squared error to derive the thickness of the films and the l-PN(THS) complex refractive index, i.e. the extinction coefficient and the (real) refractive index.

Figure 5.9 shows the optical constants of *l-PN(THS)* in the spectral region from 250 nm to 1000 nm. The extinction coefficient, *k*, trend is in excellent agreement with the absorption spectrum in Figure 5.8 (absorption coefficient, $\alpha = 4\pi k / \lambda$). In addition, the real part of the complex refractive index, *n*, exhibits two relative maxima where the first derivative of the extinction coefficient is higher as predicted by Kramers-Kronig relations and decreases significantly immediately after the relative maximum.



Figure 5.9: Complex refractive index, n + ik, of *l-PN(THS)*, derived by spectroscopic ellipsometry with a VASE instrument by J. A. Woollam Co Inc. Ellipsometric spectra have been fit by the combination of eight Lorentzian oscillators which reproduce analytically *l*-PN(THS) absorption spectrum.

5.3.2.2 F8BT:1-PN(THS) films

As the PL quantum efficiency of *l-PN(THS)* is low in solid-state films, I chose *poly[(9,9- di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)]*, namely F8BT, whose chemical structure is shown in Figure 5.11a, to be the host material for the NIR emitter for energy transfer considerations and to prevent aggregation quenching in solid-state. Actually, F8BT has been widely employed as host for a number of low-gap emitters in OLEDs^[17, 48] and exhibits a good spectral overlap between its emission and the absorption spectrum of *l*-PN(THS) as shown in Figure 5.10a.

Furthermore, HOMO and LUMO levels of *l-PN(THS)* measured at the University of Oxford and reported in Figure 5.10b together with HOMO and LUMO levels for F8BT as provided by ADS suggest that energy transfer may occur from F8BT to *l-PN(THS)* in order to boost the NIR emission. Indeed, resonance energy transfer (*RET*) is a quenching process since it decreases the photoluminescence intensity of the donor, i.e. F8BT, capturing an emitted photon which is absorbed by the acceptor, i.e. *l-PN(THS)*.



Figure 5.10: (a) Spectral overlap between the F8BT PL spectrum and *l-PN(THS)* absorption spectrum, both measured in air and at room temperature. PL measurements of F8BT have been carried out by exciting the sample at 405 nm. (b) Band diagram of F8BT and *l-PN(THS)* used in the blends. *l-PN(THS)* HOMO and LUMO have been measured at the University of Oxford by cyclic voltammetry and the uncertainty on their values is 0.1 eV.

The energy transfer rate depends also on the concentration of the host and guest materials in the blend. The absorption and PL spectra for pure F8BT and F8BT:*l-PN(THS)* blends for three different weight concentrations are reported in Figure 5.11. The colour of the film is dominated by the typical yellow of F8BT but becomes darker as the loading of NIR emitter increases. As shown in Figure 5.11c, F8BT absorption components peaking at 325 and 465 nm dominate the UV/Vis spectra range of the absorption spectra of F8BT:*l-PN(THS)* blends. A subtle *Q*-band contribution of *l-PN(THS)* rises for blends absorption in the spectral region between 800 and 900 nm peaking at ~875 nm, which is ~50 nm red shifted compared to the neat *l-PN(THS)* shown in Figure 5.8. The spectral red-shift can be attributed to a higher planarity and a reduced torsional heterogeneity of the oligomer when in blend with F8BT with respect to neat *l-PN(THS)* films.

PL spectra of pure F8BT and F8BT:l-PN(THS) blends are presented in Figure 5.11d. The F8BT emission which peaks at 565 nm with no other significant features over the 480-950 nm spectral range is progressively quenched in favour of the emission of l-PN(THS) thanks to the effective resonant energy transfer. As per the absorption spectra, notable red-shift occurs also for the PL spectra of F8BT:l-PN(THS) blend with the NIR maximum moving from 878 nm for the 1% l-PN(THS) blend to 894 nm for the 5% l-PN(THS) blend, which is more than 20 nm-red shifted compared to PL of neat l-PN(THS) reported in Figure 5.8 and can be explained with the increased rigidity of the oligomer in the blend with F8BT. Furthermore, the 16 nm-red-shift for more guest concentrated blends can indicate that l-PN(THS) is aggregating, whereas the minimal Stokes' shift in NIR region for the three blends may be related to the rigidity of the oligomers in blends and, together with the red-shift of the absorption spectra, recall a J-aggregated behaviour for l-PN(THS).



Figure 5.11: (a) Chemical structure of F8BT. (b) Picture of the measured solid-state films of pure F8BT and F8BT:*l-PN(THS)* blends for increasing loadings of NIR emitter in the blend. (c) Absorption spectra of pure F8BT and F8BT:*l-PN(THS)* blends measured in air at room temperature with no corrections of reflection and scattering. (d) PL spectra of pure F8BT and F8BT:*l-PN(THS)* blends measured in air at room temperature by exciting the samples with a CW diode laser emitting at 405 nm. The second order of the laser at 810 nm has been removed from plots.

Regarding the PL quantum efficiency of the measured samples, summarizing values are shown in Table 9 for pure F8BT and F8BT:l-PN(THS) blends. The overall PL quantum efficiency is progressively reduced by increasing the loading of l-PN(THS) in the blend from 54.4% for neat F8BT to 10.5% for the 5% l-PN(THS) blend. Interestingly, the PL quantum yield value in the NIR region (here considered beyond 830 nm) exceeds 2.5% for the 1% l-PN(THS) blend without adding pyridine to the blend as reported in [17] to limit the formation of H-aggregates which are poorly emissive and this value is significantly higher than PL quantum efficiency measured for neat l-PN(THS). Therefore, I will employ this blend as active layer in the all-polymer microcavity reported in the following section.

Sample	$\lambda_{PL_peak}(nm)$	η (%)	η _{NIR} (%)	
			(beyond 830 nm)	
F8BT	565	54.4 ± 5.0	0.2 ± 0.1	
<i>l</i> -PN 1.0% in F8BT	878	37.3 ± 3.5	2.6 ± 0.1	
<i>l</i> -PN 2.5% in F8BT	887	20.4 ± 1.2	2.2 ± 0.1	
<i>l</i> -PN 5.0% in F8BT	894	10.5 ± 0.2	1.5 ± 0.1	

Table 9: Summary of F8BT optical characterization pure and in blend with *l-PN(THS)*. PL peak wavelength is reported in NIR spectral region for F8BT:*l-PN(THS)* blends. η is the PL quantum efficiency over the whole spectrum and η_{NIR} is its fraction in the spectral range beyond 830 nm.

Having determined the complex refractive index of neat *l-PN(THS)* shown in Figure 5.9 and measured the absorption spectra of pure F8BT and F8BT:*l-PN(THS)* blends reported in Figure 5.11c, I carried out ellipsometric measurements on all the samples here reported spin-cast onto fused silica substrates. F8BT absorption spectrum has been reproduced by including four Lorentzian oscillators in the model. Each sample of F8BT:*l-PN(THS)* blends has been modelled by a Sellmeier transparent dispersion for the fused silica substrate and using a new model for an effective material for the blends accounting for the ratio in the blend of F8BT and *l-PN(THS)*. F8BT and *l-PN(THS)* in blend have been modelled according to the previous models obtained by neat materials by using four and eight Lorentzian oscillators, respectively.

Absorbance and ellipsometric spectra at different incidence angle of the light have been fitted together minimizing the mean squared error to derive the thickness of the blends and their complex refractive index, i.e. the extinction coefficient and the (real) refractive index. Figure 5.12 shows the optical constants of pure F8BT and F8BT:*l-PN(THS)* blends in the spectral region from 250 nm to 1000 nm. The extinction coefficient, *k*, trend is in excellent agreement with the absorption spectrum in Figure 5.11 (absorption coefficient, $\alpha = 4\pi k / \lambda$), with no reflections and scattering contributions, and exhibit a *Q*-band contribution at ~870 nm. The real part of the complex refractive index, *n*, is dominated by F8BT as expected but interestingly present a relative maximum at ~890 nm where the emission of l-PN(THS) occurs. The complex refractive index of 1% l-PN(THS) blend will be used in the study of the microcavity in the following section.



Figure 5.12: Refractive index dispersions for neat F8BT and F8BT:*l-PN(THS)* blends at different oligomer concentration in solid-state thin films in the 250-1000 nm spectral range. Ellipsometric spectra of neat F8BT and neat *l-PN(THS)* have been fit by the combination of four and eight Lorentzian oscillators, respectively, reproducing analytically F8BT and *l-PN(THS)* absorption spectra. Dispersions of the complex refractive indices of F8BT and *l-PN(THS)* have been used to model an effective material accounting for the ratio in the blend of F8BT and *l-PN(THS)* and fit the blends ellipsometric spectra.

5.3.2.3 All-polymer microcavities

The high PL quantum efficiency in NIR of the 1% *l-PN(THS)* in F8BT blend makes this material an interesting candidate as active layer of an all-polymer microcavity in order to obtain a narrow light source reshaped by the photonic structure action. As shown in Figure 5.11d, the emission of the blend lies around 880 nm, even if it is slightly moving towards lower energies in dependence of the collection angle. Therefore, during the fabrication of the DBR, concentration of PVK and CA solutions and rotation speed of spin coating for film deposition were adjusted accordingly in order to achieve an optical response of the DBR overlapped to the *l-PN(THS)* emission, i.e. with a minimum in transmittance located at about 900 nm.

Figure 5.13 shows in solid line the measured transmittance spectrum of a 25-bilayer DBR composed by alternating layers of PVK and CA overlapped to the best fitting calculated DBR

response (dashed) obtained by using TMM. The extended pattern of interference fringes in the measured transmittance spectrum of the DBR proves the quality of the fabricated structure. The TMM model built on Sellmeier equations for PVK and CA as reported in Section 4.3.1 fitted the experimental data for layer thicknesses of 137 nm for PVK and 153 nm for CA in agreement with profilometric measurements carried out during the DBR fabrication giving thicknesses as of 130 ± 10 nm and 150 ± 12 nm for PVK and CA respectively obtained over more than thirty thickness measurements. The total bilayer thickness, d, is about 290 nm and each layer fulfils the $\lambda/4$ condition in order to allow maximum constructive interference considering refractive index value of 1.64 for PVK and 1.47 for CA at 900 nm as reported in Figure 4.3.

To fabricate the microcavity, the F8BT:*l-PN(THS)* blend was spin-cast on top of the described DBR and additional 25 bilayers of CA:PVK have been added on top as sketched in Figure 5.14. Reflectance spectra of the final structure have been collected in ten different spots of the sample surface and shown overlapped in Figure 5.14 which assess an extremely high uniformity of the fabricated sample. The microcavity exhibits a photonic stop band between 860 and 960 nm which lies away from the absorption spectrum of the blends with a sharp minimum located at ~895 nm which can be assigned to the cavity mode. By using the F8BT:*l-PN(THS)* blend dispersion derived by ellipsometry reported in Figure 5.12, the reported reflectance spectra have been fitted for layer thicknesses of 140 nm for PVK, 155 nm for CA and 240 nm for F8BT: *l-PN(THS)* blend.



Figure 5.13: Measured transmittance spectrum of a 25-bilayer DBR fitted by a TMM calculated spectrum. The measured was fitted with layer thicknesses of 137 and 153 nm for PVK and CA respectively, while the thickness of the layers for the DBR measured by profilometry were 130 ± 10 nm and 150 ± 12 nm for PVK and CA respectively. Transmittance measurements have been carried out in air illuminating the sample at normal incidence with a halogen lamp and recording the spectrum in the same direction by using an Avantes spectrophotometer. On the right: A scheme of the DBR structure is shown with the bilayer thickness, d. Coloured legend for the DBR constituting materials is reported with their refractive index at 890 nm.



Figure 5.14: Scheme of the microcavity with top view of the sample highlighting measuring spots. On the right ten overlapped reflectance spectra are reported measured at normal incidence angle for a microcavity composed by two DBRs of 25 bilayers of PVK:CA in between of which 1% *l-PN(THS)* in F8BT layer of ~240 nm has been spin cast. Transmittance measurements have been carried out by using a halogen lamp hitting the sample and collecting the light with an Avantes spectrophotometer located along the same direction of the source.

Angle-resolved transmittance spectra for both *P*- and *S*-polarization assess the high quality of the microcavity. Figure 5.15 shows the contour plots of transmittance spectra as function of the incidence light angle. As predicted by Bragg-Snell law in Eq. (4.2), increasing the incidence angle the stop-band position disperses spectrally towards lower wavelengths but the experimental spectra exhibit a different behaviour for the two polarizations. Indeed, no significant changes on the stop-band width can be observed for *S*-polarization, i.e. when the electric field is normal to the plane composed by the light propagation direction and the vector perpendicular to the plane of an interface, whereas the stop-band width is reduced at Brewster's angle for *P*-polarization, i.e. when the electric field is along the plane of incidence. The Brewster's angle, which is the angle of incidence at which *P*-polarized light is ideally perfectly transmitted through the photonic structure with no reflections, is around 57° -incidence angle for the all-polymer

microcavity here measured, considering an effective refractive index of ~1.56, obtained by weighted average of refractive index and thickness of PVK and CA.



Figure 5.15: Contour plot of measured transmittance spectra of the microcavity as function of the angle of the incidence beam for P- and S- polarizations. The stop band and the defect centered at ~900 nm blue-shift for larger incidence angle according to Bragg-Snell law. Transmittance measurements have been carried out in air by keeping the halogen lamp hitting the sample and the Avantes spectrophotometer in the same direction while turning the sample.

Figure 5.16a compares the fluorescence spectra of the F8BT:*l-PN(THS)* microcavity with a reference sample in which the same F8BT:*l-PN(THS)* layer is spin-cast in between of two

PVK:CA bilayers, i.e. there is no photonic effect on the emission. Indeed, the photoluminescence spectrum of the reference structure is relatively broad with full width at half maximum of about 50 nm, whereas in the microcavity the emission of l-PN(THS) is strongly affected by the photonic structure as the PL squeezes into the cavity mode located at ~890 nm as per Figure 5.14 and is strongly reduced where the stop-band insists spectrally, especially in lower energy-side beyond 900 nm. Nevertheless, the interference fringes measured for the transmittance spectrum between 820 and 870 nm slightly modulate the emission of l-PN(THS).

The analysis of the spectral FWHM of *l-PN(THS)* PL in the microcavity against the reference sample allows one to assess a 10-fold shrinking of the PL linewidth which becomes as narrow as ~5.1 nm, hence the derived quality factor, $Q = \lambda_c / \Delta \lambda_c$, is about 180. Figure 5.16b reports the ratio between the PL spectra of the microcavity and the reference at 0° collection angle. The PL in the microcavity is enhanced by five time at 887 nm, almost suppressed within the stop band and unchanged ($EF_{PL} \sim 1$) outside of the stop-band.



Figure 5.16: (a) PL spectra at 0° collection angle of the microcavity (black) composed by two DBRs of 25 bilayers of PVK:CA with the F8BT:*l-PN(THS)* layer of ~240 nm as defect layer placed in the middle of the cavity compared with a reference sample in which the same F8BT:*l-PN(THS)* layer is sandwiched in between of two PVK:CA bilayers fabricated using the same parameters reported in Experimental methods. Inset: Schematics of the reference sample and microcavity sample. PL measurements have been carried out in air using an angle-resolved PL setup exciting the samples at 405 nm and collecting the light at 0° with respect to the Andor spectrophotometer. (b) PL enhancement factor, $EF_{PL} = PL_{cav} / PL_{ref}$, at 0° collection angle with respect to the detector peaks at 887 nm where the PL of F8BT:*l-PN(THS)* is 5-fold increased with respect to the reference sample.

Furthermore, the optical response of the stop-band and the cavity mode changes for increasing angles of incidence light. Figure 5.17 shows the effect on *l-PN(THS)* PL of the microcavity between 0° and 35° by 5°-steps. The *l-PN(THS)* PL is reshaped into a narrow peak up to 20° collection angle, whereas at 25° the stop band affects only the high-energy side of *l-PN(THS)* PL and the effect of the microcavity on *l-PN(THS)* PL disappears at 30°.



Figure 5.17: Angular dispersion of the microcavity transmittance spectra between 0° and 35° incidence angle overlapped with normalized fluorescence spectra of *l-PN(THS)* at correspondent collection angles by 5° steps cutting out the residual F8BT contribution to PL at higher energies. Transmittance measurements have been carried out in air by keeping the halogen lamp hitting the sample and the Avantes spectrophotometer in the same direction while turning the sample. PL measurements have been carried out in air exciting the samples (both the microcavity and the reference) with a *ps*-pulsed diode laser emitting at 405 nm and changing the collection angle of the detector accordingly.

In order to demonstrate the good quality of the fabricated microcavity and the reproducibility of the deposition process, Figure 5.18 reports the superimposition of PL spectra of *l-PN(THS)* measured on twenty-four spots of a microcavity sample surface of $3x3 \text{ cm}^2$. The PL peak is located at 890.7 ± 2.4 nm and the linewidth of *l-PN(THS)* PL (*FWHM*) is 6.4 ± 0.7, which is slightly higher than the best sample here reported. The derived *Q*-factor is 140 ± 13 which is in very good agreement with previously reported microcavities, although slightly lower than the best all-polymer microcavity ever reported.^[95]



Figure 5.18: Superimposed PL spectra of an example *l-PN(THS)* microcavity measured in 24 spots regularly spaced (4 mm) in the central area of the sample surface at 0° collection angle with histograms reporting statistic data on PL peak wavelength, linewidth (*FWHM*) and derived *Q*-factor. PL measurements have been carried out in air using an angle-resolved PL setup exciting the samples at 405 nm and collecting the light at 0° by using an Andor spectrophotometer.

Finally, with the aim of verifying whether radiative and non-radiative rates of *l-PN(THS)* change when the active F8BT:*l-PN(THS)* layer is incorporated within an optical microcavity, PL quantum efficiency and temporal evolution measurements have been carried out. The increase in PL QY of the microcavity to 3.5 ± 0.3 % compared to the reference structure (2.5 ± 0.2 %) by using an integrating sphere and following the method reported in [107], having excited both the

samples at 405 nm has been corroborated by the variation of the temporal decay for *l-PN(THS)* in the blend with F8BT, measured in air and at room temperature by a single photon counter sensitive in the NIR region, exciting the samples at 400 nm. The measured PL wavelength for the temporal decay has been chosen having measured PL spectra of the sample in the NIR region and observed the modulation of the *l-PN(THS)* PL in the microcavity which is squeezed into the defect mode at about 890 nm.

No fluence dependency of the spectral PL reshaping into the microcavity was recorded but a higher signal-to-noise ratio (*SNR*) for higher fluence, e.g. 50 μ W, was less reliable as photobleaching of the *l-PN(THS)* PL upon exposure to the pumping laser was noticed. Therefore, Figure 5.19 shows the temporal decay of the *l-PN(THS)* PL in the reference and in the microcavity measured at low fluence of 5 μ W at 890 nm, where the PL is enhanced as reported in Figure 5.16. The quality of the signal at 890 nm is higher in the microcavity than in the reference (~5 times > *SNR*) demonstrating the experimental enhancement of the PL in the microcavity. Eventually, the suppression of the *l-PN(THS)* PL in the microcavity at the stop-band edges does not allow a high enough *SNR* for the lifetime measurement at more wavelengths within the stop-band.

However, the PL decays in Figure 5.19 have been fitted by a mono-exponential expression, such as $I(t) = A + B_1 e^{-\frac{t}{\tau_1}}$. τ_l represents the decay time of the singlet exciton at 890 nm and no other contribution to photoluminescence have been found. I assess reduction of the exciton lifetime by ~17% from 0.80 ± 0.04 ns in the reference to 0.66 ± 0.03 ns in the microcavity. The lifetime for *l-PN(THS)* PL in the reference is in agreement with the PL temporal decays measured for the full class of *l*-Pn(THS) oligomers and reported in a submitted paper on *l*-P6(THS) OLEDs where we show that decay lifetime decreases from $\tau = 1.9$ ns to $\tau = 1.0$ ns (± 0.1 ns) with the increase of the oligomer length from *l-P1(THS)* to *l-P6(THS)*, respectively. Using Eq. (2.2), I derived the radiative, k_R , and non-radiative, k_{NR} , decay rates as per Table 10, demonstrating an increase by ~70% of the radiative rate for *l-PN(THS)* in the microcavity. The non-radiative rate is unchanged within experimental uncertainty.



Figure 5.19: PL decay of *l-PN(THS)* in the reference (black) and in the microcavity (red) measured at 890 nm (cavity mode) at 0° collection angle, pumping the samples with a fluence of 5 μ W at 400 nm where F8BT absorbs.

Table 10: PL quantum efficiency, η , and PL lifetime, τ , measured at 890 nm of *l-PN(THS)* in the reference and the microcavity and derived radiative, k_R , and non-radiative, k_{NR} , rates, calculated with the model proposed in the text.

Wavelength (nm)	η (%)	τ (ns)	$k_{R} (10^{8} \text{ s}^{-1})$	$k_{NR} (10^8 \text{ s}^{-1})$
890 nm (cavity mode)				
Reference	2.5 ± 0.2	0.80 ± 0.04	0.31 ± 0.05	12.1 ± 3.3
Microcavity	3.5 ± 0.2	0.66 ± 0.03	0.53 ± 0.08	14.6 ± 3.9

5.4 Conclusions

In conclusion, I presented the optical, electrical and morphological characterization of a class of NIR emitters such as linear zinc porphyrin oligomers, l-Pn(THS), newly synthesised with longer THS side chains to prevent aggregation. Here, no addition of non-aggregating agents was required for l-PN(THS), i.e. the longest oligomer of the class, in order to obtain high NIR

efficiencies. I reported all-polymer microcavities incorporating *l-PN(THS)* in blend with F8BT and fabricated by spin coating. The photoluminescence of *l-PN(THS)* in microcavities with quality factor of about 180 shows a 5-fold enhancement at the cavity mode located at 890 nm and a reduction of ~10 times for the PL full width at half maximum while the PL is suppressed at the edges of the cavity mode within the stop-band. The PL average lifetime has decreased by 17% in the cavity mode inducing an increase of the radiative rate by ~70% and this effect can be ascribed to the variation of the photonic density of states and is technologically of interest for Li-Fi communications.

6 High-Quality Porous Silicon Microcavities

6.1 Introduction

All-polymer photonics is a viable route towards the integration of photonic devices into a well-established technology platform. The use of polymers allows the design of a myriad of structures which can cover any functionality and enables the fabrication of large-area flexible devices. Nevertheless, every technology platform for inorganic photonics relies on a wellconsolidated material, e.g. silicon, indium phosphide, etc. which has been studied deeply and for which fabrication processes and yields have been built up at industry level. However, an organic material able to cover any kind of specific design requirement has not been found for photonics as of now and a plethora of outstanding applications are actually material-specific. Therefore, the use of silicon as background material not just for electronics but also for photonics has attracted significant interest for the straightforward and technologically robust fabrication techniques.

In particular, porous silicon (PSi)^[163] has gained huge attention in the field of optical sensing^[164, 165] and biosensing^[166, 167] in the last two decades, thanks to the ease of preparation via controlled electrochemical dissolution of crystalline silicon at room temperature. In addition, porous silicon photonic structures are intriguing for light management and photonic applications, due to the high quality in optical structure fabrication coupled with the possibility to infiltrate effectively a wide range of emitting materials in ambient condition exploiting its porosity. Indeed, the proportionality between the etching current density and the mass of silicon removed, allows to set finely PSi porosity and profile and, in turn, to tune accurately its refractive index by simply tuning current density value and waveform over time.^[168-170] This is a key advantage over other porous architectures^[171-177] (e.g. nanoparticles, zeolites or opals), for which there is a very limited control of the refractive index and poor accuracy in their assembling into resonant optical structures, which could give rise to defects and inhomogeneity resulting in low-quality photonic properties. In this scenario, the PSi renaissance has led to the fabrication of a large variety of photonic structures spanning from mesoporous architectures (e.g. Bragg reflectors (DBRs)^[178, 179]

resonant cavities^[180, 181], rugate filters^[182, 183], waveguides^[184]), to gradient refractive index (GRIN)^[185] optical elements to control light propagation in 2D and 3D operating both in the visible and near-infrared regions. However, although the high-quality of such photonic structures permit to achieve strong light emission modification of emitter compounds,^[186, 187] the presence of silicon, which has a strong absorption in the visible spectrum, has limited the applicability of these PSi optical structures to the (near) infrared region.

Furthermore, thanks to the intrinsic porosity of these photonic structures (in the order of 60-70%, with pore sizes spanning from few nanometres to a hundred), it is possible to infiltrate them with a large variety of active materials, such as molecules or polymers. In this regard, hybrid silicon-organic structures have already extensively reported in the literature, but in most cases the preparation involved the synthesis in situ of the desired molecule, by means of hydrosilylation or organosilanization. Although the efficiency of those processes is relatively high (in terms of pore filling and/or target molecules bonding), their applicability is limited to a relatively narrow set of monomers, and therefore not generally applicable.

For this reason the preparation of hybrid Si/SiO₂-organic structures via a solution processable method is more attractive.^[188] Interestingly, the group of Prof. Barillaro at University of Pisa found that layer-by-layer (LbL) technique offered an easy and inexpensive process for the coating of the nanometric pores, allowing to incorporate within the porous structures the target emitting molecules. In fact, with the LbL technique the ultra-thin films are formed by depositing layers of oppositely charged materials (e.g. polyelectrolytes) with wash steps in between. This technique permits a fine tuning of the coating parameters leading to homogeneous layered structures and it is also applicable to a variety of substrates of any shape, it is environmentally-friendly and it allows room temperature processing and low-cost manufacturing.^[189-191] Polyelectrolyte layered films have been used for different application, spanning from biomedical application,^[192, 193] optoelectronic^[194] and photonics.^[195]

6.2 Experimental methods

Fabrication of microcavities. Porous silicon (PSi) microcavities (MCs) have been prepared by Dr. Valentina Robbiano, in the group of Prof. Giuseppe Barillaro, at Department of Information Engineering of University of Pisa, Italy. PSi microcavities have been fabricated by anodic etching of highly doped p-type silicon (boron-doped, $\langle 100 \rangle$ -oriented, resistivity of 0.8–1.2 m Ω cm, Siltronix, Inc.) using a solution of HF(48%):EtOH, 3:1 v/v. The electrochemical etching was performed in a home-made Teflon cell using a two-electrode configuration, with the silicon substrate (area of 2.835 cm²) placed onto an aluminium flat anode (working electrode) and a platinum wire immersed in the solution and acting as cathode (and used as pseudo-reference electrode). A source-measure unit (Keithley 2410 Source Meter) was used to set the desired etching current density and to monitor the voltage drop between the silicon sample and the pseudo-reference electrode.

As first step a porous silicon sacrificial layer was prepared using a constant current density of 300 mA/cm² for 20 s and subsequently it was dissolved in a NaOH(1M in deionized (DI) water):EtOH, 9:1 v/v solution. This step is necessary to avoid the presence of a top parasitic layer which is made of pores with a small diameter (less than 50 nm) that would limit penetration of large molecules inside the structure. After NaOH dissolution, silicon samples are thoroughly rinsed with deionized water and ethanol and dried under nitrogen flow. After parasitic layer removal, the MCs are prepared by electrochemical etching with a square-wave current density profile to obtain a periodic PSi material featuring two different porosities and, in turn, two different refractive indices. Specifically, we used 300 mA/cm² and 30 mA/cm² and the defect layers are made with a current densities of 30 mA/cm², but with an increased layer thickness.

Such etching currents density waveform produce mesostructured porous silicon samples with porosity values of 61% and 78%, for the etching currents 300 mA/cm² and 30 mA/cm², respectively, and, in turn, with periodic refractive index: $n_{30mAcm2} = 1.52$ and $n_{300mAcm2} = 1.28$ at 555 nm, yielding a contrast of 0.24. The values of porosity (defined as the ratio between void volume in the microcavity and total volume of the microcavity) and, in turn, of the effective

refractive index have been estimated from the experimental reflectivity spectra of porous silicon layers etched with constant current density of either 300 or 30 mA/cm², according to the procedure described in the work by Ruminski *et al.*^[196] As for reference, random porous structures that do not feature any photonic effects with a constant etching current of 100 mA/cm² have been also prepared. All the samples have been then rinsed with isopropanol and pentane, and dried under nitrogen flow to obtain a crack-free porous layer. Eventually, samples have been thermally oxidized in a muffle furnace (ZB 1, ASAL) at 750 °C for 1 h with a ramp rate of 12 °C/min in ambient condition.

A polyelectrolyte polymer, *poly(allylamine hydrochloride)* (PAH, Mw = 45,000) synthesised at Surflay Nanotec GmbH, Berlin, Germany, has been covalently bonded to Rhodamine B to be infiltrated into the microcavities. The labelling degrees, i.e. the number of Rhodamines per number of polyelectrolyte monomer, was set at 1:145. The polyelectrolyte-Rhodamine solutions are prepared by dissolving 1 mg/mL in deionized (DI) water with 0.2M NaCl and 50mM sodium acetate (CH3COONa) at room temperature (RT) (pH = 5.6).

In order to evaluate the optical properties of these new material, the optical characterization of PAH-Rhodamine B (PAH-RhoB) was carried out in comparison to a solution of polyvinyl alcohol (PVA) and Rhodamine B not covalently bonded and to a solution of pure Rhodamine B, whose chemical structures are reported in Figure 6.1. Both of them were prepared using the same condition as for the covalently bonded one diluting the active materials into deionized water at 1 mg/ml concentration.

Eventually, infiltration of PAH-RhoB and PVA/RhoB into the porous silicon microcavities has been carried out via drop-casting of the polymer solutions previously characterized in air and at room temperature, resulting in a hybrid Psi/polymer resonant cavity after solvent evaporation. Fluorescence microscopy after polymer infiltration has shown good uniformity of the infiltration across the whole structure.

Optical characterization of Rhodamine B solutions. Absorption spectra were collected using an Agilent 8453 UV-Vis UVV spectrometer and quartz cuvettes for the solutions. PL

spectra were collected by an Andor Technology EMCCD (SR1 631) spectrometer, exciting the solutions by a CW diode laser (Thorlabs, $\lambda_{exc} = 520$ nm). PL efficiency has been measured by means of an integrating sphere exciting the samples at 520 nm nm following the method described in [107]. Time-resolved PL measurements were carried out exciting with a *ps*-pulsed diode laser (pulse duration = 40 ps, $\lambda_{exc} = 445$ nm) and detecting the PL with a photomultiplier coupled to a monochromator and a time-correlated single-photon counting unit (TCSPC, Edinburgh instruments, LifeSPec II, time resolution ~150 ps).

Optical characterization of Rhodamine B microcavities. Reflectance spectra have been measured by illuminating the samples with an Ocean Optics halogen lamp normally to the surface of the structure and detecting the optical response by an Avantes spectrometer. PL spectra were collected by an Andor Technology EMCCD (SR1 631) spectrometer, exciting the solutions by a CW diode laser (Thorlabs, $\lambda_{exc} = 520$ nm). The latter have been carried out by by Dr. Valentina Robbiano at the University of Pisa. Time-resolved PL measurements were carried out exciting with a ps-pulsed diode laser (pulse duration = 40 ps, $\lambda_{exc} = 445$ nm) and detecting the PL with a photomultiplier coupled to a monochromator and a time-correlated single-photon counting unit (TCSPC, Edinburgh instruments, LifeSPec II, time resolution ~150 ps). Scanning electron microscopy and fluorescence microscopy measurements have been carried out by Dr. Valentina Robbiano at the University of Pisa.

6.3 Optical properties

6.3.1 Materials characterization

In Figure 6.1, the chemical structures of (a) polyvinyl alcohol (PVA) and Rhodamine B (RhoB), (b) poly(allylamine hydrochloride) (PAH) and Rhodamine B (RhoB) and (c) Rhodamine B (RhoB) are shown. Rhodamine B is a common dye easily soluble in deionized water, also used as standard for fluorescence for orange emitters. Here, it is compared to the newly synthesised

PAH-RhoB chemically bonded with a ratio of one monomer of Rhodamine B every 145 monomers of PAH and a blend of PVA and RhoB with the same ratio (145:1) of units.



Figure 6.1: Chemical structures of (a) polyvinyl alcohol (PVA) and Rhodamine B (RhoB) blended in a ratio of 145:1 at 1 mg/ml concentration in deionized water, (b) poly(allylamine hydrochloride) (PAH) and Rhodamine B (RhoB) chemically bonded with a ratio of 145 monomers of PAH for each monomer of RhoB at diluted at 1 mg/ml concentration in deionized water and (c) Rhodamine B (RhoB).

Figure 6.2 shows the absorption and PL spectra of PAH-RhoB (red), PVA/RhoB (blue) and RhoB (green) normalised with respect to the PVA/RhoB maxima. The absorption spectra of RhoB and PVA/RhoB exhibit the lowest energy peak located at 553 nm and a secondary shoulder at about 520 nm. The absorption spectrum of the blend is spectrally unchanged compared to the pure material as well as the ratio between the two peaks (~ 3-fold more intense at 553 nm). Differently, the PAH-RhoB absorption spectrum presents both peaks slightly red-shifted with respect to RhoB and PVA/RhoB spectra and positioned at 558 nm and 530 nm, respectively, with a relative ratio of about 1.5. On the other hand, PL spectra show a well-defined band with main

peak located at 578 nm for RhoB and PVA/RhoB and at 583 nm for PAH-RhoB a secondary lower band in the red portion of the visible spectrum between 600 and 650 nm.



Figure 6.2: Normalized absorption (dashed lines) and PL (solid lines) spectra of PAH-RhoB (red), PVA/RhoB (blue) and RhoB (green) dissolved at 1 mg/ml concentration in deionized water solutions. All measurements have been carried out in air and at room temperature using transparent quartz cuvettes. PL spectra have been collected exciting the sample by a CW diode laser (Thorlabs) emitting at 520 nm (here removed from the plots where * has been located).

In Table 11 I report the estimated values for PL efficiencies, η , and PL lifetime, τ , of the diluted solutions of PAH-RhoB, PVA/RhoB and RhoB. The huge decrease of the PL efficiency of the PAH-RhoB which is about five times lower than PL efficiency values measured for RhoB and PVA/RhoB can be attributed to the increase of non-radiative phenomena such as charge transfer within the PAH-Rho polymer, which would limit its employability in real-world applications. Furthermore, the lifetime values obtained by fitting temporal decays of PAH-RhoB, PVA/RhoB and RhoB by a mono-exponential expression, such as $I(t) = A + B_1 e^{-\frac{t}{\tau_1}}$, show a slight reduction in the PAH-RhoB lifetime by ~8% compared to RhoB and PVA/RhoB. The use of a single exponential is attributed to the only species present in the measured dilute solutions, which is the singlet exciton of RhoB. No contribution of other species has been measured.

Table 11: PL quantum efficiency, η , and PL lifetime, τ , measured at 580 nm of PAH-RhoB, PVA/RhoB and RhoB in solution and their derived radiative, k_R , and non-radiative, k_{NR} , effective rates, calculated with the model proposed in the text.

Material	η (%)	τ (ns)	$k_R (10^{-8} \text{ s}^{-1})$	$k_{NR} (10^{-8} s^{-1})$
PAH-RhoB	5.4 ± 0.1	1.67 ± 0.03	0.33 ± 0.07	5.66 ± 0.31
PVA/RhoB	24.3 ± 0.7	1.79 ± 0.04	1.36 ± 0.10	4.23 ± 0.22
RhoB	27.6 ± 0.7	1.80 ± 0.04	1.53 ± 0.11	4.02 ± 0.23

6.3.2 PSi microcavities

Figure 6.3a shows the typical reflectance spectrum of an as-made PSi microcavity (red line) composed by two DBRs of 20 bilayers, with a stop band whose full width at half maximum is about 130 nm, reflectance of ~90% and centred at 725 nm as suggested by the typical reddish colour of the structure in the inset photo. The large width of the reflectance band and the absence of the cavity modes are due to the higher refractive index of the silicon, i.e. the higher index contrast between silicon and air, at this stage of the microcavity fabrication for which a $\lambda/2$ condition for the cavity mode is not verified, hence the cavity mode is hindered. Figure 6.3b shows a scanning electron microscopy (SEM) cross-section image of the as-made structure with a thicker defect layer sandwiched between the two symmetric DBRs, with a magnified area close to the defect layer where darker and brighter regions indicate high and low porosity layers.

After the oxidation process (blue line), the photonic stop-band move by ~125 nm towards lower wavelengths as expected by the reduction of the index contrast between the oxidised silicon and air, here considered as high and low refractive index media. The full width at half maximum is reduced to 90 nm and the structure exhibits a typical greenish colour as per the relevant inset photo. Furthermore, a high reflectance is still measured as well as a good quality of the photonic structure is preserved upon oxidation as demonstrated by regular interference fringes. A sharp cavity mode appears at about 600 nm with a full width half maximum as narrow as 2.5 nm which allows to estimate a Q-factor of ~240.

By contrast, Figure 6.3c reports the reflectance spectra of the reference random porous silicon sample, as-made (red line) and oxidised (blue line), with no photonic features visible. The SEM cross section confirms the absence of any periodicity in the reference sample as per Figure 6.3d.



Figure 6.3: Reflectance spectra of (a) a porous silicon microcavity as-made and after oxidation with relevant pictures of the samples in insets and (d) a random porous structure as-made and after oxidation not showing any photonic effects. Scanning electron microscopy (SEM) cross-section images of (b) an as made PSi microcavity with 20 bilayers on both sides of the defect layer and (d) an as made random porous structure. The magnified inset in (b) shows alternating darker/brighter regions which correspond to high and low porosity layers, hence low and high refractive index layers, respectively.

The infiltration of the photonic structures after oxidization with the emitting polymer is carried out via drop-casting overnight, in air and at room temperature, as sketched in Figure 6.4. As the previous optical characterization of the blend PVA/RhoB and pure RhoB resulted in very similar spectroscopic features, here I report results for porous silicon microcavities infiltrated only by PAH-RhoB and PVA/RhoB. Both polymers solutions have been diluted in order to have the same Rhodamine B units as ratio with PAH and PVA respectively and infiltrate the microcavities uniformly across their thickness as demonstrated by fluorescence microscopy after solvent evaporation in Figure 6.5, where cross-section images for microcavities are shown upon infiltration.



Figure 6.4: Sketch of the infiltration process. The as-made sample (red circle) is oxidized first changing its optical response (green circle), then infiltrated by drop-casting of PAH-RhoB and PVA/RhoB.



Figure 6.5: Fluorescence images of the cross sections of (a) an oxidized PSi microcavity infiltrated by PAH-RhoB and (b) an oxidized PSi microcavity infiltrated by PVA/RhoB, taken by Dr. Robbiano. Both structures are homogeneously infiltrated as per the uniform fluorescence emission over the whole thickness.

Several batches of porous silicon microcavities have been fabricated, infiltrated and characterized optically. Despite a good reproducibility of the stop-band spectral localisation, the optical response of each microcavity is extremely sensitive to the fabrication parameters, however the most significant features are unchanged. In first instance, upon the infiltration of the microcavities with the active polymer the photonic stop-band of the structure red-shifts by ~20 nm for the variation of the refractive index contrast. Indeed, the air pores are now filled up by the emissive material which has a higher refractive index, hence the effective medium refractive index, expressed as weighted sum of the different materials which compose the photonic structure, tends to increase and the stop band moves towards higher wavelengths as expected by Bragg-Snell law. Secondly, the infiltrated microcavities show a spectral widening of the defect mode both in reflectance and PL spectra due to the variation in the refractive index contrast which induce a concomitant reduction of the cavity quality factor, $Q \sim 150$.

Figure 6.6 shows the optical response of two microcavities infiltrated by (a) PAH-RhoB and (b) PVA/RhoB, whose PL, overlapped to the reflectance spectrum, is strongly reshaped by the photonic structure. Herein, for both materials a comparison with PL spectra of the relevant random porous silicon structure is presented. The stop-bands of the microcavity are well-defined and exceed ~90% reflectance with a sharp defect mode located at 613 nm for PAH-RhoB and 637 nm for PVA/RhoB, respectively. However, the interference fringes are better resolved in Figure

6.6a, which exhibits the expected periodicity on both sides of the stop-band. Nevertheless, both the PL spectra exhibit a very narrow feature in correspondence of the cavity mode, a large suppression of PL where the stop band insists spectrally and a slight enhancement at the photonic stop band edges, especially at lower wavelengths. By contrast, the PSi reference acts as simple interferometer which does not affect in any way the PL of the active material, except than for the typical periodic modulation.

Comparing the PL spectra of the microcavities with their relevant samples, an enhancement by ~50% for the polymers emission has been measured at the cavity mode due to the rearrangement of the photonic density of states. On the other hand, within the stop-band, the PL of both active materials is evidently suppressed as expected by the optical response of the photonic crystal. The lower efficiency of PAH-RhoB, as reported in Table 11, determines a lower signal-to-noise ratio of its PL spectrum, however in both cases the PL spectra are almost unchanged compared to solutions in Figure 6.2.



Figure 6.6: Reflectance spectra (black lines) and PL spectra (red lines) at 0° collection angle of a microcavity composed by two DBRs of 20 bilayers infiltrated by (a) PAH-RhoB and (b) PVA/RhoB superimposed to the PL spectra of a random porous silicon reference (blue lines) infiltrated by the same materials. Transmittance measurements have been carried out by using a halogen lamp and collecting the reflecting light with an Avantes spectrophotometer using a Y-optical fiber. PL measurements have been carried out in air using an angle-resolved PL setup exciting the samples at 520 nm and collecting the light at 0° by using an Andor spectrophotometer.
As further mean to testify the good quality of the fabricated structures, the PL spectra of the microcavities shown in Figure 6.6 and infiltrated by (a) PAH-RhoB and (b) PVA/RhoB have been measured by changing the collection angle. Figure 6.7 shows the contour plots of normalized PL spectra for the references (a-c) and the microcavities (b-d) infiltrated by PAH-RhoB (a-b) and PVA/RhoB (c-d), respectively, as function of the collection angle. In both cases, while the reference samples exhibit an unaffected PL spectrum due to the emitters embedded within a random interferometer, in the microcavity the enhanced peak of PL at cavity mode (at 613 nm for PAH-RhoB and 637 nm for PVA/RhoB, respectively) at 0° collection angle blue-shift by ~50 nm as the collection angle increases up to 30° as predicted by the Bragg-Snell law. Similarly, the band-edge peak for both infiltrated microcavities follows the exact same trend. The microcavity effects on PL spectra decreases beyond 35° where the stop-band overlaps only the high-energy band of the PL spectrum of PAH-RhoB and PVA/RhoB.



Figure 6.7: Contour plots of normalized PL spectra for the reference (a-c) and the microcavity (b-d) infiltrated by PAH-RhoB (a-b) and PVA/RhoB (c-d), respectively, as function of the collection angle. PL measurements have been carried out in air exciting the samples (both the microcavity and the reference) with a CW diode laser emitting at 520 nm and changing the collection angle of the detector accordingly.

To gain a further insight in the porous silicon microcavity photophysics, the PL radiative decays of PAH-RhoB and PVA/RhoB infiltrated in the reference and in the microcavity are shown in Figure 6.8. As per their angle-resolved PL spectra reported in Figure 6.7, the reshaping of PL is dispersive with the collection angle as the microcavity stop-band blue-shifts when measured at larger angles. Therefore, cavity modes previously measured at 613 nm for the PAH-RhoB microcavity and 637 nm for the PVA-RhoB microcavity at 0° collection angle (Figure 6.6) blue-shift accordingly by 25 nm as expected by the dispersions in Figure 6.7. This is due to the

geometrical arrangement in the PL lifetime setup for PL decays collection as the samples undergo a $\sim 21^{\circ}$ collection angle.

Indeed, the cavity modes are located at 588 nm for the PAH-RhoB microcavity and 612 nm for the PVA-RhoB microcavity, where PL decays have been measured as shown in Figure 6.8. Additional PL temporal decay measurements have been carried out on both edges of the microcavities stop-band where the PL is suppressed, i.e. at 570 nm for PAH-RhoB and 594 nm for PVA/RhoB (high-energy side of the stop-band, SB) and at 600 nm for PAH-RhoB and 630 nm for PVA/RhoB (low-energy side of the stop-band, SB). In the cavity mode (CM) both the active materials incorporated within the microcavities exhibit a faster decay time than their correspondent references, which are not expected to provide any photonic effect on the PL of infiltrated polymers.

PL decay time constants and relative contributions to PL of PAH-RhoB and PVA/RhoB in the reference structure and in the microcavity are reported in Table 12, as obtained by fitting PL decays in Figure 6.8 by a bi-exponential expression, $I(t) = A + B_1 e^{-\frac{t}{\tau_1}} + B_2 e^{-\frac{t}{\tau_2}}$. Once again, the large surface/volume ratio of the regions in which the polymers have been infiltrated has a strong influence on the photophysical properties of the emitters. As reported in the literature,^[111, 197-199] two lifetimes for conjugated polymers can be attributed to strongly bound intramolecular excitons (primary exponential, τ_1) and weakly bound interchain states (secondary exponential, τ_2) due to polymer aggregates or to the polymer interaction with the SiO₂ nanostructure.

A clear modification of PL lifetimes in microcavities can be observed with respect to the reference samples for both the polymers, but the lifetime values are not comparable for the two materials as expected by their PL efficiencies in solution (5.4% for PAH-RhoB vs 24.3% for PVA/RhoB). The different host of RhoB results in different evaporation time and arrangement of polymers upon infiltration which changes the photophysics properties of these materials. In particular, in the cavity modes I observed a reduction by ~28% for τ_1 and ~19% for τ_2 for PAH-

RhoB at 588 nm and by ~1% for τ_1 and ~15% for τ_2 for PVA/RhoB at 612 nm, which confirm the rearrangement of the density of states inside the cavity at the resonance wavelength.

Furthermore, the redistribution of the photonic density of states is corroborated by observing a slower decay lifetime of the PL of both materials outside of the cavity modes but within the microcavity stop-band. An increase of lifetimes has been measured at lower wavelengths (high-energy side of the stop-band) by ~28% for τ_1 and ~15% for τ_2 for PAH-RhoB at 570 nm and by ~23% for τ_1 while unchanged for τ_2 for PVA/RhoB at 594 nm. Similarly, at higher wavelengths (low-energy side of the stop-band) I noticed a rise in the PL lifetime by ~31% for τ_1 and ~22% for τ_2 for PAH-RhoB at 600 nm and by ~14% for τ_2 while unchanged for τ_1 for PVA/RhoB at 630 nm. Eventually, the relative contribution of the two species to PL are quite uniformly constant across different measured wavelengths and structures except at higher wavelengths where the very low emission of infiltrated polymers compromises the actual estimate of the ratio between the two components.

The evidence of the reduction of PL lifetimes within the cavity modes in porous silicon microcavities is a clear demonstration of the modification of the density of states. However, the silicon substrate on which these structures have been fabricated prevented the measurement of the PL quantum efficiency of microcavities and relevant references as per the method reported in [107] in order to derive the variation of radiative and non-radiative rates. In fact, the high contribution to absorption of silicon under 650 nm does not allow to evaluate the PL efficiency variation between the microcavity and the reference and a fully transparent structure detached by the silicon substrate as shown in [199] would accommodate this experimental measure. Nevertheless, the reduction of PL lifetimes in the cavity modes indicates the enhancement of the spontaneous emission rate for the emitter due to the environment,^[200] therefore proves the suitability of these structures for lasing as demonstrated by Robbiano et al. for a blue-emitter such as *poly*(9,9-*di*-*n*-octylfluorenyl-2,7-*diyl*), known as F8 or PFO.^[199]



Figure 6.8: Experimental (exp) PL decays of PAH-RhoB (left) and PVA/RhoB (right) in the reference (PSi, blue lines) and in the microcavity (MC, red lines) measured at 570 nm for PAH-RhoB and 594 nm for PVA/RhoB (high-energy side of the stop-band, SB), at 588 nm for PAH-RhoB and 612 nm for PVA/RhoB (in the cavity mode, CM) and at 600 nm for PAH-RhoB and 630 nm for PVA/RhoB (low-energy side of the stop-band, SB). All measurement were taken in air and at room temperature positioning the samples with a collection angle of ~ 20° with respect to the detector and exciting the samples by a ps-pulsed laser emitting at 445 nm.

	Wavelength (nm)	τ_1 , ns (I ₁)	$ au_2$, ns (I ₂)
	570 nm (high-energy side stop-band)		
PAH-RhoB	Reference	$1.06 \pm 0.01 \; (0.53)$	$2.96 \pm 0.02 \; (0.47)$
	Microcavity	$1.36 \pm 0.02 \ (0.53)$	$3.40 \pm 0.03 \ (0.47)$
	588 nm (cavity mode)		
	Reference	$1.19 \pm 0.01 \; (0.49)$	$3.17 \pm 0.02 \; (0.51)$
	Microcavity	0.74 ± 0.01 (0.47)	$2.57 \pm 0.01 \ (0.53)$
	600 nm (low-energy side stop-band)		
	Reference	$1.30 \pm 0.01 \ (0.56)$	$3.34 \pm 0.03 \ (0.44)$
	Microcavity	$1.71 \pm 0.02 \ (0.70)$	$4.08 \pm 0.06 \; (0.30)$
PVA/RhoB	594 nm (high-energy side stop-band)		
	Reference	$1.37 \pm 0.01 \; (0.62)$	$4.48 \pm 0.02 \; (0.38)$
	Microcavity	$1.69 \pm 0.01 \; (0.52)$	$4.45 \pm 0.02 \; (0.48)$
	612 nm (cavity mode)		
	Reference	$1.57 \pm 0.01 \; (0.65)$	$4.89 \pm 0.03 \; (0.35)$
	Microcavity	$1.55 \pm 0.01 \ (0.60)$	$4.19 \pm 0.02 \; (0.40)$
	630 nm (low-energy side stop-band)		
	Reference	1.68 ± 0.01 (0.66)	$5.02 \pm 0.03 \; (0.34)$
	Microcavity	$1.68 \pm 0.01 \; (0.54)$	$4.41 \pm 0.02 \ (0.46)$

Table 12: Lifetime values, τ_1 and τ_2 , with relative contribution to PL of each species in brackets of PAH-RhoB and PVA/RhoB in the reference structure and in the microcavity derived by the fit of PL decays in Figure 6.8. The χ^2 value on all the fits is included between 1.0 and 1.1.

6.4 Conclusions

In this chapter, I reported the full optical characterization of porous silicon microcavities infiltrated via drop-casting. A newly synthesised positively charged polymer, PAH-RhoB, has been measured in comparison with PVA/RhoB blend and pure RhoB assessing a decrease in PL

quantum yield by five times, for which this synthetic approach does not represent a particularly interesting route for optoelectronic applications. However, upon the infiltration of PAH-RhoB and PVA/RhoB within nanostructured porous silicon resonant microcavities, fabricated by a low-cost and up-scalable method, I demonstrated a reshaping of the PL for both the materials with the typical optical dispersion as function of the collection angle. Finally, the reduction of PL lifetimes in the microcavities within the cavity mode with respect to the reference is ascribed to the variation of the photonic density of states.

7 Other works

7.1 Polystyrene 3D Photonic Crystals

Artificial opals have a periodic modulation of the dielectric constant in three directions and constitute a well-known system to study the optical properties of 3D PhCs. I fabricated direct opals by so-called vertical deposition as sketched in Figure 7.1a, starting from a commercially available monodisperse (standard deviation < 5%) nanospheres water suspension,^[68] with a diameter of 200 nm, diluted with de-ionized water. The solution concentration and the pulling-up velocity were relevant parameters to obtain a crystal thickness of ~ 5 μ m upon complete water evaporation. Atomic force microscopy (AFM) measurements show the presence of ~10x10 μ m² monocrystalline domains without line defects.

I measured unpolarised reflectance and transmittance spectra at increasing incidence angles. A distinct low-energy peak is blue-shifted from 455 to 370 nm, as the incidence angle θ increases, as shown in Figure 7.1. The measured stop-band central wavelength fits Eq. (4.2) for $n_{eff} = 1.40 \pm 0.06$ and $d = 200 \pm 10$ nm up to 50° (Bragg-Snell's equation). For larger angles, the shape of the reflection spectrum changes significantly and a secondary reflection peak appears for $\theta > 50^\circ$ due to constructive interferences of secondary family-planes. Such a peak "anticrosses" the main one at $\theta_K = 53.5^\circ$, where the two have the same height. θ_K is related to the details of the Brillouin zone and, via Snell's law, provides an estimate of n_{eff} and d.^[201] In our case, I find $n_{eff} = 1.39 \pm 0.01$ and $d = 202 \pm 1$ nm.

Polarized reflectance and transmittance spectra for vertical polarization are qualitatively similar to the unpolarised spectra, whilst the horizontal polarization spectra present a reflectance peak collapse at an incidence angle of 54.5° , corresponding to Brewster's angle at the interface between air and opal. Within the effective index approximation, this provides a further estimate of the opal effective index ($n_{eff} = 1.40 \pm 0.01$), in good agreement with the previous ones.

The study of the dependence of the optical properties of direct opals on the polarization has been included in the paper "*Polarization Studies of a 3D Photonic Crystal using Transmission*

and Reflection Experiments", now submitted, and useful for the optical characterization of direct opals infiltrated by conjugated polymers, carried out in the group of Prof. Cacialli.



Figure 7.1: (a) Sketch of the vertical method for the fabrication of direct opals with an atomic force microscopy image of an area $10x10 \ \mu\text{m}^2$ measured on the opal surface. (b) Unpolarised reflection spectra for incidence angles θ from 15° to 60° in 5° steps. Inset: Reflection spectra for θ from 45° to 60°.

7.2 Novel red/NIR polymeric host for OLEDs

Thanks to a collaboration with the group of Prof. Wang of the University of Chalmers, a modified BTT emitter and a novel red/NIR polymeric host (PIDT-2TPD, a novel indacenodithiophene-based polymer) were blended by Dr. A. Minotto, obtaining the best ever reported values of external quantum efficiency for a pure NIR emitter from a polymer-based light-emitting diode (PLED) based on a heavy-metal-free, solution-processed active layer, as reported in the paper "*Efficient Near-Infrared Electroluminescence at 840 nm with "Metal-free" Small-molecule:Polymer Blends*", Advanced Materials, 2018.^[49]

Within the work for the above paper, I measured the refractive index and extinction coefficient spectra of PIDT-2TPD, shown in Figure 7.2, via ellipsometry (Horiba Jobin-Yvon MM16, wavelength region 430-850 nm at 70° incidence angle). The analysis has been carried out on a 140 nm thin film spin-coated on a silicon substrate, fitting Ψ and Δ spectra with four-Lorentz

oscillator model. The accuracy of the fit has been verified further by comparing the fit extrapolated thickness with those measured with a Dektak profilometer $(140 \pm 3 \text{ nm})$ and atomic force microscopy (AFM) (138 ± 4 nm). The measurement of the refractive index enabled the correct estimation of the external quantum efficiency of NIR OLEDs reported in the paper.



Figure 7.2: Refractive index (n, black line) and .extinction coefficient (k, red line) of PIDT-2TPD measured via ellipsometry (Horiba Jobin-Yvon MM16, wavelength region 430-850 nm at 70° incidence angle). The analysis was carried out on a 140 nm thin film spin-coated on a silicon substrate, fitting Ψ and Δ spectra with a four-Lorentz oscillator model. The accuracy of the fit was verified further by comparing the fit extrapolated thickness with those measured with a Dektak profilometer (140 ± 3 nm) and atomic force microscopy (AFM) (138 ± 4 nm).

7.3 Optically switchable organic light-emitting transistors

Organic light-emitting transistors (OLETs) are pivotal components for emerging optoelectronics applications, such as logic circuitries and smart displays. Within this technology sector, the integration of multiple functionalities in a single electronic device remains the key challenge. In the work "*Optically switchable organic light-emitting transistors*", born from a collaboration with the group of Prof. Paolo Samorì (University of Strasbourg) and Prof. Stefan

Hecht (University of Berlin), published on Nature Nanotechnology^[8], we have reported the fabrication and characterization of the first optically switchable organic light-emitting transistors (OSOLETs), by integrating photochromic molecules into the light-emitting semiconducting layer of OLETs via simple solution processing. Both charge transport and electroluminescence (EL) have been simultaneously modulated by irradiating the devices at distinct wavelengths. We have demonstrated three classes of OSOLETs emitting over the entire visible spectrum (green, red, and blue), which can reversibly and remotely switch charge transport and EL on and off via visible and UV light irradiation. For this work I designed and built with Giovanni F. Cotella and Prof. Franco Cacialli the device characterization setup and performed the quantitative OLET device characterization.



Figure 7.3: (a-c) EL spectra and emitting images of F8T2/DAE_tBu, MDMO-PPV/DAE_tBu and F8/DAE_F OSOLETs. (d-f) Transfer characteristics of F8T2/DAE_tBu OSOLET (Vd = -100 V), MDMO-PPV/DAE_tBu OSOLET (Vd = -120 V) and F8/DAE_F OSOLET (Vd = -100 V), and light-triggered current switching upon UV and visible light irradiation. (g-i) Luminance and light-triggered switching of the luminance in green, red and blue OSOLETs upon UV and visible light irradiation.

8 Conclusions and Outlook

The organic photonics breakthrough will rely on novel and performing materials and on reliable and cheap technologies, which can enable the transition from academia to industry.

In this thesis I have reported my findings on conjugated polymers suitable for photonic applications and demonstrate their use into low-cost photonic structures useful for optical communication and sensing.

In Chapters 2-3 I have shown for the first time the full characterisation of an aggregationinduced emitter, such as a phenylated derivative of PPV, namely PDPV, which boosts its PL quantum efficiency from the solution to the aggregated solid-state film. Upon the addition of a non-solvent for PDPV, such as 2-propanol (IPA), to the toluene solution, the PL quantum efficiency increases dramatically (~60 times) and, simultaneously, the PL lifetime becomes longer, when IPA content in the mixture is higher, which lowers the non-radiative rates by 96% thanks to the restriction of intramolecular rotations as final demonstration of the occurrence of the aggregation-induced emission for PDPV.

Such impressive rise of PL quantum efficiency makes PDPV an ideal active material for organic light-emitting diodes. I have reported the full optical characterization of PDPV in blend with PVK using an approach never used before for PDPV increasing its PL efficiency. Due to the high solid state efficiency of PDPV, I have presented *EQE* values for PDPV:PVK OLEDs improved by 50% compared to pure PDPV with lower turn-on voltage and higher radiances.

The basic characterization of PDPV has revealed its potential for real-world application thanks to the high quantum efficiency in solid state. The good external quantum efficiency reported in this dissertation can be further improved by optimizing the essential vertical structure employed in this thesis, working both on the geometrical arrangement and the engineering of electrodes. Nevertheless, PDPV may be engineered as host for efficient energy transfer on low gap emitters in the near infrared. Beyond their use for optical communications, an obvious area of development for AIE polymers is represented by fluorescent sensors which may exhibit excellent sensitivity and ease of operation for the straightforward working principle. Also PDPV may be functionalized in order to recognise analytes and turn-on fluorescence as the lateral phenyls have their rotations restricted, especially if used in solution where the large variation in PL quantum efficiency can enable the measurement of very low level of analytes. In this field, biomarkers for in vitro diagnosis of diseases can be of great interest for medicine, given the biocompatibility of AIE materials.

In the second part of this thesis I have investigated the use of conjugated polymers into all-polymer flexible microcavities.

In Chapter 4 I have reported on all-polymer microcavities doped with PDPV through a low-cost fabrication process based on spin coating, demonstrating an enhancement of the photoluminescence of PDPV by ~13 times at the cavity mode and a reduction of ~18 times for the PL full width at half maximum while it is suppressed at the edges of the cavity mode. Simultaneously, the PL average lifetime has decreased in the cavity mode compared to the reference sample and increased in the stop band. The decrease of the PL average lifetime at the cavity mode has induced an increase in the radiative emission rate and this effect can be ascribed to the variation of the photonic density of states.

Similarly, in Chapter 5, I have presented the optical, electrical and morphological characterization of a class of near-infrared (NIR) emitters such as linear zinc porphyrin oligomers, *l-Pn(THS)*, newly synthesised with longer THS side chains to prevent aggregation. I have shown the optical characteristics of all-polymer microcavities incorporating the longest porphyrin oligomer in blend with F8BT. The photoluminescence of the NIR emitter in microcavities with quality factor of about 180 shows a 5-fold enhancement at the cavity mode and a simultaneous reduction of ~10 times for the PL full width at half maximum while the PL is suppressed at the edges of the cavity mode within the stop-band. The PL average lifetime has decreased in the cavity mode inducing an increase of the radiative rate by 70% and this effect is attributed to the

variation of the photonic density of states and is technologically of interest for Li-Fi communications.

All-polymer microcavities offer low fabrication costs and high scalability, however they are limited by the small index contrast achievable with polymers. An area of future interest for polymer photonics is the employment of novel dielectric materials able to increase the index contrast, therefore allowing the strong coupling regime which is also limited by the planarity of these structures. In these regards, a further development of the work here presented is the incorporation of multidimensional functional defects which may enhance the effect on the density of states and eventually lower the lasing thresholds. Both two-dimensional patterning in the plane of the active layer with techniques such as scanning thermal lithography and scanning near-field optical lithography can be exploited as well as soft-lithographic transfer which may represent a further step towards industrial production.

Beyond the technological enhancement for the field, DBRs and microcavities apply to a wide range of applications spanning from large area emitters and lasers, low-cost disposable sensors, colorimetric safety devices and transparent photovoltaic modules. Actually there is only the imagination of scientists which can limit the infinite applications where flexible low-cost photonic devices can become a breakthrough.

In the last part of this thesis, I have reported the full optical characterization of porous silicon microcavities infiltrated via drop-casting by a novel Rhodamine B-derivative. Nanostructured porous silicon resonant microcavities have been fabricated by a low-cost and upscalable method and I have demonstrated a reshaping of the PL and the reduction of PL lifetimes in the microcavities within the cavity mode with respect to the reference which I ascribed to the variation of the photonic density of states.

A monolithically integrated silicon microcavity such as the structure here reported as proof of concept represents a building block for silicon photonics which has recently gained renewed interest. The use of silicon limits the applications of this structures in the full visible range though, therefore recently a silica-on-silicon approach to photonic integration has been considered boosting the benefits of the established fabrication processes at industrial level for silicon and the physical advantage for losses of silica. The further advantage derived from the incorporation into these structures of conjugated polymers, notable for their high photoluminescence, represents a potentially disruptive novelty. Future outlook for the field is the implementation of large scale fabrication processes towards a new generation of photonically-enhanced chips with advanced features for microfluidic systems and biosensing.

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