LIGHT AMPLIFICATION IN ORGANIC SELF-ASSEMBLED NANOAGGREGATES

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CHAPTER 1

INTRODUCTION
AND WORK PLAN

The interest in organic materials for optoelectronics and photonic applications has significantly increased in recent years. Basic planar devices, like thin-film light emitting diodes, transistors, photovoltaic cells, lasers, and sensors have been successfully demonstrated. Among the emerging class of low-cost organic materials, conjugated oligomers are short, linear chain molecules with the potential to form ordered assemblies with low trap densities and high carrier mobility (up to ~ 20 cm$^2$V$^{-1}$s$^{-1}$) [1]. In many of such systems, charge transport joins with outstanding optical properties: a high absorption/emission cross section, an optical gap tunable from the ultraviolet to the visible, and a high emission quantum yield. Light amplification has been observed in several oligomers [2], even though it is still uncertain whether a suitable combination of transport and optical properties can lead to the realization of an all-organic electrically pumped laser.

Conventional methods to grow molecular crystals can be considered as a kind of self-assembly, mediated by weak van der Waals interactions [3]. In that way, macroscopic crystals in the centimeter length scale with atomic-scale order can be grown. Although of interest for the
investigations of intrinsic material properties, bulk systems are of limited importance for many applications, which require the use of flat thin films over macroscopic surfaces. In thin films, self-assembly is governed by a subtle competition between the weak interactions among molecules and the interaction with the substrate. The resulting dynamics of molecular aggregation is not only difficult to control, but also to predict, due to the inherent limitation of computational methods to describe lattice configurations that may differ by as little as a few kJ/mol. As a matter of fact, the considerable advancements made in recent years [4], have been driven by empirical rules and material scientists’ intuitions. Thanks to these efforts, crystalline film engineering typically permits to grow polycrystalline specimens with domains in the micrometer scale. Microcrystallinity is detrimental to the optical and transport performances. In high quality films, mobility is actually limited by inter-domains charge transport. From the point of view of the optical response, the high density of surface defects could result in the decrease of the luminescence efficiency, while large propagation losses arise from light scattering at the grain domain interfaces [5].

Recently, it has become clear that the assembly of organic films can be directed by specific interface interactions. In the last decade, a large number of organic molecules have been investigated for their ability to self-assemble in well-organized nanostructures that turned out to be important for applications in photonics [6], optoelectronics [7] and chemical sensing [8]. The most studied light-emitting molecules for these purposes are oligomers of thiophene [9], phenylene [10], tetracene [11], and perylene-tetracarboxilic dianhydride aromatic rings [12].

Deposition of oligophenyls and oligothiophenes on substrates featuring strong surface dipoles, such as mica and potassium chloride, has been shown to lead to self-assembly of highly ordered aggregates through the occurrence of a dipole induced-dipole interaction mechanism [13]. Needle-shaped aggregates are formed with lengths of up to 1 mm and cross-sectional dimensions (widths and heights) of the order of 100 nm [13-15]. X-ray diffraction studies show a high degree of epitaxial alignment; the long molecular axes are nearly parallel to the substrate and perpendicular to the needle axis [16]. Upon substrate contamination and subsequent modulation of the surface electric field, morphologically diverse nanoaggregates can be obtained, e.g., ring-shaped structures (microrings) [17]. Nanoaggregates can be also transferred to other substrates more suitable for device fabrication. Encouraging results along this direction have been recently reported [18-20], which could allow one to imagine mesoscale self-assembly by using molecular aggregates as elementary bricks [21].

Linear nanoaggregates usually referred to as nanofibers, display a number of important optical properties, i.e., strong optical anisotropy, both in absorption and emission [14], optical waveguiding in the visible spectrum [20,22,23], optical up-conversion [24], Raman gain
amplification [25], nonlinear spectral narrowing [23,26]. Another basic photonic functionality still to explore is light amplification, which could further enlarge the horizon of the potential applications of self-assembled molecular nanoaggregates in photonics and optoelectronics. Organics are indeed excellent gain media with emission cross section as high as $10^{15} \text{ cm}^2$ [27]. Being one-dimensional self-assembled light waveguides, nanofibers actually appear ideal to support light amplification by stimulated emission radiation (LASER).

As already stated by many Authors [28], the term "laser" represents, however, a too general concept to provide insight on the complex and subtle nonlinear optical instabilities observed in nature when stimulated emission processes are intrinsically linked to optical feedback. In conventional lasers, this latter is provided by suitable distributed optical elements; the resulting process of light amplification differ considerably from the one observed in various gain media, like inorganic semiconductor powders [29], rods [30] and needles [31], epitaxially grown inorganic semiconductor layers [32], dye infiltrated synthetic opals [33], biological tissues [34], high-gain organic films based on polymers [33,35] and small molecules [36]. In these systems recurrent optical amplification is provided by random optical discontinuities of the system itself. The complex interplay among stimulated light scattering, feedback and photon localization has recently been the subject of several theoretical and experimental studies [28,37]; coherent and incoherent random lasing are intriguing concepts introduced to account for the different photons statistics in disordered systems. Incoherent random lasing could be thought as a generalization of the notion of Amplified Spontaneous Emission (ASE), in presence of nonresonant feedback.

In this thesis, we focus on the study of light amplification in para-sexiphenyl ($p$-6P) nanofibers. The process of self-assembling introduces an intrinsic degree of disorder, which causes light scattering and random feedback. We demonstrate the occurrence of “lasing”. The major experimental effort has been addressed to reveal coherent and incoherent random lasing, through a suitable control of nanofiber disorder, and to correlate the inherent optical response to the aggregate morphology at the micron and submicron scales, using combined optical and atomic force microscopy.
The thesis is structured as follows:

In chapter 2, we review the molecular exciton theory. Peculiarities of the emission properties of molecular aggregates are discussed.

In chapter 3, we present the experimental techniques used to grow the \textit{p-6P} samples studied in this work. Quasi-epitaxial growth of nanofibers on polar dielectric surfaces is discussed. Basic optical emission properties of \textit{p-6P} single crystals and nanofibers are presented.

In chapter 4, we briefly overview the atomic force microscope set-up used to study the morphological properties of \textit{p-6P} nanofibers as well as the experimental set-up used in spectrally- and spatially- resolved photoluminescence and lasing measurements.

In chapter 5, we present the experimental results of ensemble-averaged and spatially-resolved photoluminescence measurements on both close-packed and isolated nanofibers. Experimental findings on random lasing and amplified spontaneous emission are discussed. The influence of sample morphology on the optical response is experimentally investigated on the micrometer scale. The emission gain cross section of \textit{p-6P} nanofibers is assessed. A simple theoretical approach to model one-dimensional random waveguide light resonances in nanofibers is presented.

Chapter 6 is devoted to the summary of the results. Prospect applications of nanofibers in photonics and optoelectronics are outlined.
2.1. Introduction

The name of organic semiconductors generally indicates a wide class of materials, aggregates of carbon-based molecules of different length (oligomers and polymers). Their electronic and optical properties make them belong to the semiconductor category, but inside this class of materials an enormous multiplicity of behaviour exists, which is very difficult to generalize.

Molecular solids are composed of discrete molecules held together by weak van der Waals forces; they are generally soft with low melting point and poor electrical conductivity. Because of the weak nature of the van der Waals bonding, it is to be expected that the properties of the single molecule are retained in the solid state. This expectation is basically realized, even though the intermolecular interactions in the crystal play an important role [38]. A study of the excitonic and electronic properties of molecular semiconductors must therefore start with a review of the electronic properties of the individual molecules.
The electronic ground state configuration of carbon atom is 1s^22s^22p^2, with four electrons in the outer electronic levels; the two s electrons are paired and the two p electrons are unpaired. Another possible, but less stable, electronic configuration for the carbon atom can be generated by mixing the 2s and the 2p orbitals, creating a set of four equivalent degenerate orbitals, called sp^3 hybrid orbitals. In this way, the carbon atom can make four tetrahedral bonds like in methane molecule. It is also possible that the 2s and two 2p orbitals (2p_x and 2p_y for example) combine to form three planar hybrid orbitals sp^2. This type of hybridization is at the base of the electronic and optical properties of organic semiconductors. The three sp^2 orbitals are coplanar and directed about 120° apart from each other; bonds formed by these orbitals are called σ bonds. The 2p_z orbital, unaltered by the hybridization, is perpendicular to the plane of the sp^2 orbitals and can lead to the formation of the π-type bonds by overlapping the neighbouring p_z orbitals (Figure 2.1.a).

![Diagram of σ and π bonds between two carbon atoms.](image)

*Fig. 2.1. (a) Schematic representation of σ and π bonds between two carbon atoms. (b) Energy level diagram of the carbon atoms and of the formed molecule.*

The π bond establishes a delocalized electron density above and below the plane of the σ bonds, with no electron density in the nodal plane, coinciding with the plane of the molecule. The degree to which the π-electrons cloud of one molecule is delocalized and interacts with
Chapter 2: Organic molecular semiconductors

those of the neighbour molecules in the solid state represents a crucial problem to understand the collective properties of the molecular crystals.

In studying the electronic properties of molecular solids, it will be sufficient to focus on the properties of the $\pi$ electrons. These latter indeed are in the highest-energy occupied orbitals (Figure 2.1.b) and therefore they are the most easily excitable.

2.2. Exited states in molecular crystals: the excitonic model

2.2.1. The physical dimer

In order to introduce the molecular excitonic model, we first discuss a simpler system, the physical dimer. This name is used to describe two identical molecules spatially close to each other that do not form any chemical bond between themselves.

The Hamiltonian operator for the physical dimer can be written as:

$$H = H_1 + H_2 + V_{12}$$

where $H_1$ is and $H_2$ are the Hamiltonian operators for the isolated molecules and $V_{12}$ is a perturbative term representing the intermolecular interaction.

Neglecting the vibrational and spin part, the ground state wavefunction of the dimer is:

$$\Psi_G = \Psi_1 \Psi_2$$

where $\Psi_1$ and $\Psi_2$ are the ground state wavefunctions of the single molecules.

The solution of the Schrödinger equation, in the first order perturbation theory, gives the ground state energy of the dimer:

$$E_G = E_1 + E_2 + W$$

with $W = \langle \Psi_1 \Psi_2 \mid V_{12} \mid \Psi_1 \Psi_2 \rangle$

where $E_1$ and $E_2$ are the ground state energies of the monomers and the last term $W$ is the coulombic binding energy of the van der Waals interaction for the pair, which is negative for the dimer and positive for the excimer.

Because of the presence of term $V_{12}$ representing the intermolecular interaction in the Hamiltonian, the excitation energy is shared between the two molecules and the excited-state dimer wave function can be written as a linear combination of the unperturbed states:

$$\Psi_E = c_1 \Psi_1^* \Psi_2 + c_2 \Psi_1 \Psi_2^*$$

where $\Psi_1^*$ and $\Psi_2^*$ are the equivalent excited states of the two identical molecules forming the dimer. Solving the Schrödinger equation for the excited state

$$H( c_1 \Psi_1^* \Psi_2 + c_2 \Psi_1 \Psi_2^*) = E_E( c_1 \Psi_1^* \Psi_2 + c_2 \Psi_1 \Psi_2^*)$$

in the case of identical molecules ($E_1^* = E_2^*$), the energies of the first excited states for the dimer can written as:
\[ E_{E}(\pm) = E_{1}^{*} + E_{2} + \langle \Psi_{1}^{*} \Psi_{2} V_{12} | \Psi_{1}^{*} \Psi_{2} \rangle \pm \langle \Psi_{1}^{*} \Psi_{2} V_{12} | \Psi_{2}^{*} \Psi_{1} \rangle = E_{1}^{*} + E_{2} + W' \pm \beta \]

The term \( W' \) is the coulombic energy of interaction between the charge distribution of the excited state of the molecule 1 and that of the ground state of the molecule two (or vice versa) and it leads to an energy shift relative to the monomer states. The last term \( \beta \) is the resonance interaction energy term and it causes a splitting of the excited state in the dimer (Figure 2.2).

The corresponding wavefunctions for the first excited states are:

\[ \Psi_{E}(\pm) = \frac{1}{\sqrt{2}} (\Psi_{1}^{*} \Psi_{2} \pm \Psi_{2}^{*} \Psi_{1}) . \]

Fig. 2.2. Splitting of the excited state of the dimer and energy shift relative to the monomer.

The previous model has been strongly simplified by neglecting the antisymmetrization of the wave functions required by the Pauli exclusion principle. This would have introduced an exchange interaction term that is negligible for singlet spin states but becomes very important for triplet spin states [38,39].

### 2.2.2. Molecular crystals

The extension of the excited state model of the physical dimer to a molecular crystal does not introduce particular difficulties. Neglecting the vibrational and spin part, the ground state wavefunction for a system composed by \( N \) identical non-interacting molecules is:

\[ \Psi_{G} = \prod_{n=1}^{N} \psi_{n}^{0} \]
Considering only electrostatic interactions, the Hamiltonian operator can be approximated as the sum of the Hamiltonian of individual molecules $H_0$ and the term of intermolecular interactions $V$ between all the pairs of molecules in the solid:

$$H = \sum_n H_n + \sum_{n\neq m} V_{nm} = H_0 + V$$

The model can be simplified considering a linear unidimensional lattice with one molecule per unit cell and imposing periodic boundary conditions. The excited state wave function of the crystal can be written as a linear combination of the unperturbed states and the variational principle allows to calculate the best possible coefficients of this combination. If only the nearest-neighbours interactions are considered, the exciton wavefunction with wavenumber $k$ is:

$$\Psi_k = \frac{1}{\sqrt{N}} \sum_{l=1}^{N} e^{ikd} \Psi'_l$$

where $\Psi'_l$ are the unperturbed degenerate wavefunctions, $d$ is lattice constant and the wavenumber $k$ can takes the values $0, \pm 2\pi/Nd, \pm 4\pi/Nd,..., \pm \pi/d$. The eigenvalues corresponding to these $N$ states are:

$$E(k) = E_0 + \delta\omega_0 + 2\beta \cos(kd)$$

where $E_0$ is the molecular electronic transition energy, $\beta$ is the interaction energy between neighbouring molecules and can be positive or negative, and $\delta\omega_0 = \delta\epsilon - \delta\omega$ is the energy shift (see Figure 2.3).

Fig. 2.3. Energy level scheme illustrating the shifts of the ground and of the first excited states in the crystal relative to the case of non-interacting molecules (gas phase). The width of the exciton band $4|\beta|$ is indicated.
The crystal excited-states described above are called Frenkel excitons or tight-binding excitons.

In general, a given molecular energy level splits into as many exciton bands as there are inequivalent molecules per the unit cell. For example, if we consider a crystal with \( n = 2 \), the spectrum will be composed by two bands, each of one having a \( k \) band states, as shown in Figure 2.4.

The separation between the two bands at \( k = 0 \) is called Davydov splitting and depends on the interaction between the translationally inequivalent molecules, whereas the \( k \)-dispersion of each band depends on the interaction between equivalent molecules. The Davydov splitting for singlet exciton can reach several thousand of \( \text{cm}^{-1} \), while it is of the order of \( 10 \ \text{cm}^{-1} \) for triplet excitons [38,39].

2.2.3. Transition dipole moments: H and J aggregates

In the model of the physical dimer, the resonance interaction energy term \( \beta \) causes a splitting of the excited states. In the dipole-dipole approximation, this interaction term can be expressed, in the case of two molecules per unit cell, as a function of the transition dipole moment of the isolated molecules, \( \vec{\mu}_1 \) and \( \vec{\mu}_2 \):

\[
\beta = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} = \frac{\vec{\mu}_1 \cdot \vec{r}}{r^3} \left( \frac{\vec{\mu}_2 \cdot \vec{r}}{r^3} \right)
\]
where $\vec{r}$ is the position vector of the dipole of molecule 2 relatively to the molecule 1. The sign of $\beta$ depends on the mutual orientation of $\vec{\mu}_1$ and $\vec{\mu}_2$. The transition dipole moment of the two resulting Davydov components is given by the vector sum of individual transition moment:

$$M = \frac{1}{\sqrt{2}} (\vec{\mu}_1 + \vec{\mu}_2).$$

We can distinguish three different configuration depending to the relative orientations of $\vec{\mu}_1$ and $\vec{\mu}_2$: a) Parallel; b) Head-to-tail; and c) Oblique (Figure 2.5 a, b and c respectively).

In the case of parallel transition dipole moments (Figure 2.5.a), the out-of-phase configuration leads to an electronic attraction ($\beta < 0$), producing the $E^+\ast$ state. Since the dipole moment $M$ is null, the transition from the ground state to exciton state $E^+\ast$ is forbidden. The in-phase arrangement causes repulsion ($\beta > 0$), giving the $E^-\ast$ state. In this case the dipole moment $M$ is non-null and the transition from the ground state to exciton state $E^-\ast$ is dipole allowed. Therefore, for parallel dipole alignment, the lowest electronic transition is forbidden and the emission and absorption spectrum of the crystal is blue shifted with respect to the isolated molecules. Molecular solids that present this arrangement are called $H$ aggregates.

![Fig. 2.5. Transitions from the ground state to the Davydov exciton bands for three different arrangements of the molecular transition dipole moments: parallel (a), head-to-tail (b) and oblique (c). Orientation of the monomer dipole moments is represented by short arrows. Dipole-forbidden and allowed transitions are depicted by dashed and continuous arrow respectively.](image)

When the transition dipole moments of the two molecules are arranged in the head-to-tail configuration (Figure 2.5.b), the in-phase orientation leads to the $E^+\ast$ state while the out-of-phase gives the $E^-\ast$ state. Since the dipole moment is non-vanishing for the transition from the
ground state to the $E^+$ state and is null for the transition to $E^-$ state, only the first excitonic transition is dipole allowed. Therefore, in this type of arrangement, the emission and absorption spectrum of the crystal is red shifted with respect to the isolated molecules. Molecular solids with this type of dipolar coupling are called $J$ aggregates.

In the third case of oblique transition dipole arrangement (Figure 2.5.c), the in-phase orientation leads to the $E^+$ state, while the out-of-phase gives the $E^-$ state. In this case, the dipole moments for the electronic transition from the ground state to the Davydov bands are both non-vanishing. Therefore, both transitions are radiative.

2.3. Light emission properties of H aggregates

Most of the conjugated oligomers relevant for optoelectronic applications (phenyls, thiophenes, phenylene-vinylenes, and oligoacenes) crystallize in the so-called herringbone (HB) structure [40-43], in which the molecular dipoles are nearly parallel. Recent photoluminescence studies performed on high quality single crystals or films, illustrative of the intrinsic optical response of this class of compounds, show a weak pure excitonic transition, intense vibronic bands, and quantum yields as high as several tens per cent [44-47].

The following paragraph is mainly devoted to the discussion of the fundamental radiative emission properties of band-edge excitons in prototypical HB aggregates.

2.3.1. Emission properties of herringbone molecular aggregates: a theoretical model

In the last few years, F.C. Spano developed the theory on the optical properties of pinwheel aggregates (Figure 2.6.c), which are precursors of the herringbone lattice [48-51].

The model studies the absorption and emission properties of a simplified square lattice $M \times M$, with $N = M^2$ molecules of $p$-distyrylbenzene (DSB) in the positions $(n_x, n_y)$, $(n_x, n_y = 0, 1, 2, \ldots, M-1)$, with lattice constant $d$, in the chiral and achiral configurations (Figure 1.6 d and c). The molecules are supposed to have only two states: the ground state $1^1A_g$ and the excited state $1^1B_u$ with electronic transition frequency $\omega_{00}$. This transition is coupled linearly to an intramolecular and totally symmetric vibrational mode at frequency $\omega_0$. The $1^1A_g$ and $1^1B_u$ nuclear potentials for a given molecule are assumed harmonic, with the same curvature but with the minima shifted. The vibrational state of the electronic ground state are represented as:

$$|g; m_{(0,0)}, m_{(1,0)}, \ldots, m_{(M-1,M-1)}\rangle,$$

with energy $\hbar \omega_0 \sum_n m_n$, where $m_n$ is the number of vibrational
quanta of the molecule $\vec{n}$ and $|g\rangle$ is the electronic part of the ground state of the aggregate, in which all the molecules are in the state $1^1A_g$.

![Figure 2.6](image)

Fig. 2.6. (a): DSB molecular structure with two possible orientations of the transition dipole moment. (b): Component of the transition dipole moments in the herringbone plane (x-y plane) for the two orientation of the molecule. (c): Perpendicular components of the transition dipole moment in a 2×2 pinwheel chiral aggregate. (d): 4×4 chiral type aggregate. (e): 4×4 achiral type aggregate [49].

The Hamiltonian for such a system can be written as:

$$H = \hbar \omega \sum_{\alpha} b_{\alpha}^+ b_{\alpha} + \hbar \omega \lambda \sum_{\alpha} (b_{\alpha}^+ + b_{\alpha}) |\vec{n}\rangle \langle \vec{n}| + \sum_{\alpha} \sum_{\beta} J_{\alpha\beta} |\vec{n}\rangle \langle \vec{m}| + \hbar \omega_0 + D + \lambda^2 \omega_0$$

where $\hbar = 1$ is taken; $b_{\alpha}^+$ ($b_{\alpha}$) is the creation (annihilation) operator for the intramolecular vibrational mode on the molecule $\vec{n}$; $|\vec{n}\rangle$ is the pure electronic state in which the molecule in the site $\vec{n}$ is in the excited state $1^1B_u$, while all the others are in the ground state; $D$ is the energy shift induced by the van der Waals interaction with the neighbouring molecules in the aggregates; $\lambda^2$ is the Huang-Rhys factor, that accounts for the electro-vibrational coupling; $J_{\alpha\beta}$ is the excitonic coupling between the molecules in the sites $\vec{m}$ and $\vec{n}$.

The eigenstates of $H$, giving the $\alpha$-th vibrationally dressed exciton with wave vector $\vec{k}$, can be written as:

$$|\alpha;\vec{k}\rangle = N^{\frac{1}{2}} \sum_{\vec{n}} |\vec{n}\rangle e^{i\vec{k}\cdot\vec{n}} G_{\vec{n}}^\alpha \sum_{l_{0,1}(0,1)l_{0,1}} C_{l_{0,1}l_{0,1}}^{\alpha} \left\{ \prod_{l=0}^{\infty} (l_{0,1})^{(0,1)l_{0,1}} \right\}$$
Light amplification in organic self-assembled nanoaggregates

where $\tilde{I}_n(t, \ldots)$ is the number of vibrational quanta in the excited (ground) state of the molecule in the site $n$; $G_G^{\alpha \beta}$ are the shift operator that moves the vibrational excitation to the right by $n_x$ units and up of $n_y$ units, respectively.

The dipole moment operator for the transition $1^1A_g \rightarrow 1^1B_u$ can be written as:

$$\mu = \sum_n \left( \mu_{x,n} \hat{i} + \mu_{y,n} \hat{j} + \mu_{z,n} \hat{k} \right) \left| g \right\rangle \left\langle n \right| + \text{h.c.}$$

$\mu_{x,n} = \pm \frac{i}{2} \mu_\perp (1 + (-1)^{n_x})$ and $\mu_{y,n} = \pm \frac{j}{2} \mu_\perp (1 - (-1)^{n_y})$ are the $x$ and $y$ components of the transition dipole moment of the molecule in the site $n$, where the $\pm$ sign indicates the molecular orientation, and $\mu_\perp$ and $\mu_\parallel$ are the components perpendicular and parallel to the long molecular axis, respectively.

According to the Kasha rule, the exciton recombination takes place from the bottom of the exciton band, that is from the state $\left| n,d; \alpha \right\rangle$ to the $p$-th vibrational state of the electronic ground state, with transition energy $\omega_{\alpha p}$.

The fluorescence spectrum can be written as:

$$S_F(\omega) = \sum_{p=0,1,2, \ldots} I_p \left( 1 - \frac{p\omega_0}{\omega_{\alpha 0}} \right)^3 W(\omega - \omega_{\alpha 0} - p\omega_0)$$

where $W(\omega - \omega_{\alpha 0} - p\omega_0)$ is a symmetric line shape function representing homogeneous and inhomogeneous broadening, and $I_p$ is the dimensionless intensities of the $0$-$p$ transition:

$$I_p = \frac{1}{\mu_\perp^2} \sum_{n,m=0,1, \ldots} \left| \left\langle \alpha_n^*, \beta_n^* \right| g; m_{(0,0)}, m_{(0,1)}, \ldots \right\rangle \left\langle \alpha_n^*, \beta_n^* \right| \right|^2$$

When the excitonic coupling is weak compared to the vibrational frequency $(\sum_n (-1)^{n_x}J_{\alpha_n^*, \beta_n^*}) < \omega_0$, the coefficients $c_{\alpha_n^*, \beta_n^*}$ of the eigenstates $\left| \alpha_n^*, \beta_n^* \right\rangle$ approach the unity and the line intensity become:

$$I_p = \delta_{p,0} \frac{\left\langle \alpha_0^*, \beta_0^* \right| \left. \right| \left\langle \alpha_0^*, \beta_0^* \right| \left\rangle \left\langle \alpha_0^*, \beta_0^* \right| \left. \right|}{N \mu_\perp^2} \left( \sum_n \mu_{x,n} \left| 1 \right|^2 + \sum_n \mu_{y,n} \left| 1 \right|^2 + (1 - \delta_{p,0}) \left( 1 - \frac{\mu_\parallel^2}{\mu_\perp^2} \right) \left( \left\langle \alpha_0^*, \beta_0^* \right| \left. \right| \right) \right)^2$$

where $\left\langle \alpha_0^*, \beta_0^* \right| \left. \right| \left\langle \alpha_0^*, \beta_0^* \right| \left. \right| = \frac{2^p e^{-2\hat{x}^2}}{p!}$ is the molecular Frank-Condon factor.
The previous equation shows that, in the free exciton limit ($\lambda^2 = 0$), the lowest exciton band is non emissive if $\mu_\perp = 0$. The 0-0 transition ($p = 0$) is allowed only when $\mu_\perp \neq 0$, and is polarized entirely in the x-y plane. Conversely, the vibronic replicas ($p \neq 0$) are present in the emission spectrum if $\lambda^2 \neq 0$, are configuration independent and are polarized primarily along the z axis (for $\mu_\parallel^2 > \mu_\perp^2$).

The intensity of the emission for the pure electronic transition can be written in a more general form as:

$$I_0 = \frac{F}{N\mu_\perp^2} \left\{ \sum_{n} \mu_{x,n}^2 + \sum_{n} \mu_{y,n}^2 \right\}$$

where $F = \sum_{\alpha,\pi} \langle 0 | \mathbf{T}_{\alpha,\pi} | 0 \rangle \alpha_{\alpha,\pi}^{x}(x,x) \alpha_{\alpha,\pi}^{x}(x,x)$ is the generalized Franck-Condon factor, which ranges from $e^{-\lambda^2}$ in the weak exciton-phonon coupling to 1 in the strong coupling regime. $I_0$ is vanishing for the chiral type aggregates (fig.2.6.d), where the transition dipole moments interfere destructively, while reach the maximum value $NF\frac{\mu_\parallel^2}{2\mu_\perp^2}$ in the achiral type (fig.2.6.e), where the x and y components of the transition dipole moments add in phase.

Figure 1.7 shows how the intensity of the 0-0 transition for achiral-type ($I_0^B$) aggregate and of the vibronic replicas for achiral ($\sum_{p=0} I_0^B$) and chiral ($\sum_{p\neq0} I_0^d$) aggregates changes with the excitonic coupling strength [49].

$I_0^B$ increases with rising of the excitonic coupling, whereas the intensity of the vibronic replicas is configuration independent and diminishes with increasing excitonic coupling. Unlike $I_0^B$, the intensity of the vibron transitions is not enhanced by $N$.

An increase of coupling reduces the nuclear displacement of the emitting state thereby reducing the effective aggregate Huang-Rhys factor $\lambda^2$. In this case, the 0-0 transition is favoured with respect to the vibronic replicas but, on the other hand, it is weakly dipole allowed only if $\mu_\perp \neq 0$. This effect leads to a decrease of the radiative decay rate and therefore to a reduction of the luminescence quantum yield of the crystal respect to that of the isolated molecules.
In the low exciton coupling regime, the emission of the herringbone aggregate is dominated by the vibronic progression while the pure electronic transition is weakly present or null if $\mu_\perp = 0$. In this case the luminescence quantum yield of the crystal approximates the one of the isolated molecule. In general, however, any type of site defect could make the 0-0 emission allowed also in the chiral-type aggregate [50].

Comparison with experimental results confirms the conclusion of the theoretical model. Figure 2.8 shows the emission spectrum of DSB film as well as the calculated fluorescence spectrum averaged over uniform random distribution of molecular orientation in a 4×4 aggregate [36]. The weak 0-0 band is found to be polarized in the aggregate x-y plane, while the strong vibronic progression is predominantly z-polarized. The intensity of the 0-0 peak is found to be variable because it depends on the distribution of molecular orientations. The disappearance of the pure electronic transition in some samples may simply due to the preponderance of chiral-type aggregates in which the x-y dipole moment vanishes.
Fig. 2.8. Comparison of the experimental DSB fluorescence (filled circles) taken at 20 K with the calculated fluorescence (solid curve), using $\mu_\perp/\mu_\parallel = 0.11$ [49].
CHAPTER 3

SELFASSEMBLED
PARA-SEXIPHENYL NANOFIBERS

The samples investigated in this thesis are films of self-assembled nanofibers of \textit{para}-sexiphenyl molecules, grown on freshly cleaved muscovite mica substrates by both OMBD and HWE techniques. In this section, we review the properties of both the \textit{p}-6P molecule and crystal, as well as the process of self-assembling of \textit{p}-6P to form crystalline nanostructures.
3.1. Para-sexiphenyl single crystal

Para-sexiphenyl (C_{36}H_{26}) is an aromatic linear chain molecule consisting of six benzene rings (Figure 3.1). The oligomer is thermally stable up to 300-400 °C and can be synthesised with high grade of purity. Crystals of p-6P molecules are classified as p-type semiconductors with remarkable optical and electronic properties, among which, a bright photoluminescence (photoluminescence quantum yield is ~ 30%) [44-47] in the blue visible range and a high hole mobility (field effect mobility ~ 10^{-1} \text{cm}^2\text{V}^{-1}\text{s}^{-1}) [52].

![Fig. 3.1: Para-sexiphenyl (p-6P) molecule.](image)

Para-sexiphenyl usually crystallizes in the β-phase, which has a monoclinic unit cell belonging to the space group P2\_1/a, with lattice constants of a = 8.091 Å, b = 5.565 Å, c = 26.264 Å, a monoclinic angle β = 98.17° (Figure 3.2 a) [53]. The unit cell contains two molecules.

![Fig. 3.2. (a): Monoclinic unit cell of crystalline p-6P; a,b and c are the lattice constants. (b): Arrangement of the p-6P molecules within the β structure; molecules form layers with thickness of 25.97 Å. (c): Projection of the molecules along their long axis showing the herringbone structure within each layer [10].](image)

In the crystal, p-6P molecules are organized in layers with thickness of 25.97 Å (Figure 3.2 b). The long molecular axes are aligned forming an angle of 73° with respect to the layer basal plane. At room temperature, the average conformation of p-6P molecules is planar [10]. Figure 3.2 (c) shows the projection of the molecular planes on a single layer. Nearby molecular planes are tilted by about 66° each other, forming the typical herringbone structure.
3.1.1 Optical transitions

Para-sexiphenyl crystals form a herringbone-type H aggregate with two translationally inequivalent molecules per unit cell. According to Davydov's theory (§ 2.2.2), the lowest unoccupied orbital of the \( p-6P \) molecule gives rise to two exciton states at the centre of the Brillouin zone (fig. 3.3). Taking into account that the component of the molecular transition dipole in the herringbone plane is null (\( \mu_\perp = 0 \)), the simple radiative annihilation of the lowest Davydov exciton is dipole-forbidden. However, the exciton decay with simultaneous creation of ground-state C=C stretching phonons is allowed and polarized along the long molecular axis of the \( p-6P \) molecule (§ 2.3.1).

![Exciton levels energy scheme](image)

Fig. 3.3: Exciton levels energy scheme of the \( p-6P \) free molecule and crystal, with the lowest forbidden (0-0) and allowed (0-1, 0-2, 0-3) optical transitions. The arrows on the right of the exciton bands indicate the orientation of the molecular dipole moments for the transition to the ground state.

The absorption and emission spectra of a polycrystalline \( p-6P \) film deposited on glass substrate are shown in Figure 3.4 [54]. Due to the presence of structural defects, the pure electronic transition (0-0) is detected in the emission spectrum, even though much weaker than the vibronic replicas (0-1, 0-2, 0-3). The photoluminescence quantum yield is as high as 30 % [44-47], suggesting that excitons are in the weak coupling regime, in which the light emission efficiency of the crystal approaches that of the isolated molecule (see Figure 2.7, § 2.3.1).
Finally, it is worth stressing that the forbidden nature of the 0-0 transition leads to a large Stokes-shift between the lowest absorption band and the luminescence spectrum. Such optical response of near-gap excitations is peculiar of H-aggregates and permits to reduce the reabsorption of the light emitted by the crystal, and thus, to lower lasing threshold.

3.2. Growth techniques of \( p-6P \) nanoaggregates

Thin films of \( p-6P \) are prepared by physical vapour deposition (PVD) in high vacuum (HV) and ultra high vacuum (UHV). The high thermal stability of the molecules allows the sublimation by thermal evaporation without any dissociation of the molecules. Two different PVD techniques are employed to grow the samples studied in this thesis: Organic Molecular Beam Epitaxy (OMBE) has been used by the group of Prof. H.G. Rubahn (University of Odense, Denmark), and Hot Wall Epitaxy (HWE) by the group of Prof. H. Sitter, (University of Linz, Austria). In both techniques, the \( p-6P \) films are grown on muscovite mica substrates.

3.2.1. Organic Molecular Beam Epitaxy

Figure 3.5 shows a schematic representation of the MBE apparatus. Thin sheets of mica (thickness \( \sim 120\mu m \)) are cleaved in air and transferred immediately after cleavage into a high vacuum transfer chamber \( (p \approx 10^{-7} \text{ mbar}) \). A second high vacuum chamber \( (p \approx 10^{-8} \text{ mbar}) \) is used for the deposition process only. The substrates are mounted on a copper plate which allows homogeneous heating via a tungsten filament, and are carefully outgassed for an hour at a temperature of \( \sim 400\text{K} \) before the organic material is deposited. Para-sexiphenyl molecules are deposited at temperature above 600K by vacuum sublimation from a Knudsen cell type oven (nozzle diameter 0.5 mm and pressure during the deposition \( \approx 2\times10^{-7} \text{ mbar} \)) with deposition rates of \((0.1 - 0.3) \text{ Å/s, and at a substrate temperature of (350-360) K. A water-cooled quartz microbalance system (QMS) allows to measure the deposition rate and the nominal thickness of the deposited film.}

Fig. 3.4: Absorption and emission spectra of \( p-6P \) deposited on glass substrate [54].
Chapter 3: Self assembled para-sexiphenyl nanofibers

Fig. 3.5: MBE apparatus used for epitaxy-growth of p-6P films. It is constituted by three different sections: (i) magnetically coupled transfer unit; (ii) deposition chamber (MBE) including the Knudsen sublimation cell and a quartz microbalance system (QMS); (iii) characterization section equipped with a multi-channel-plate low-energy electron diffraction apparatus (MCP-LEED). Pressure inside each unit is indicated.

The third section of the MBE apparatus is the characterization unit in UHV ($p \approx 10^{-10}$ mbar), equipped with a multi-channel-plate low-energy electron diffraction system (MCP-LEED, Omicron). Here, the crystallinity of the nanostructure grown on the substrate are checked. Using a very low electron flux (100 pA mm$^{-2}$), beam damage as well as charging of the surface is avoided.

Para-sexiphenyl molecules deposited on mica substrate form mutually parallel linear aggregates, with submicron-sized width and height, and length up to one millimeter. LEED, absorption and photoluminescence measurements showed that the aggregates grow nearly perpendicular to the direction of the long molecular axis of p-6P molecules deposited on the substrate [55]. The dimensions and the mutual distances between nanostructures depend strongly on the deposition rate and substrate temperature. Only at low deposition rates between 0.025 and 0.5 Å/s and in a narrow substrate temperature range $\Delta T \approx 25$ K around 400 K, formation of long nanofibers occurs [56]. At lower substrate temperatures, fibers tend to become shorter and more densely packed, whereas at higher temperatures only small islands of p-6P have been observed [13]. This allows to locally induce or avoid needle growth via laser-induced surface heating. The length of the nanofibers and their mutual distances has been controlled focusing an argon ion laser beam onto the mica substrate during the film growth [57]. With this laser-controlled growth, long and well-isolated nanofibers, like those shown in the epifluorescence micrograph in Figure 3.6, have been obtained.
3.2.2. Hot Wall Epitaxy

The second technique used to grow the $p$-6P nanofibers films studied in this thesis is the HWE. In contrast to other sublimation techniques like MBE, HWE allows to grow epitaxial layers close to the thermodynamic equilibrium, which is very important in the case of van der Waals epitaxy of organic compounds. Consequently, the organic molecules can find energetically the most suitable arrangement before being incorporated into the crystal lattice, resulting in highly ordered structures on the deposited organic layer [58]. Figure 3.7 shows the schematic representation of the HWE apparatus used to grow the $p$-6P films. The system is simpler than the MBE apparatus and needs only HV technology ($p \sim 10^{-6}$ mbar). It consists of a sublimation quartz ampoule, at the bottom of which the $p$-6P molecules, that have to be evaporated, are placed. Six separated heaters (source and wall ovens) allow independent temperature adjustments in the different regions of the evaporation quartz tube. This guarantees a nearly uniform and isotropic flux intensity and kinetic energy of the molecules. This is opposite to MBE technique, where the films are deposited by means of a uniaxial flux of molecules. The substrate is placed close to the ampoule end (at a distance of 5 mm) and can be heated independently during the growth process. Para-sexiphenyl molecules are evaporated at temperature above 600K and deposited on freshly cleaved mica substrate, with pressure during the growth $\approx 6 \times 10^{-6}$ mbar and deposition rates of 0.3 Å/s. The wall temperature was usually in the range of 350-500 K, and the substrate temperature 400 K. As in MBE, the substrate temperature during evaporation and the deposition rate are fundamental parameters for molecular packing in the solid-state structures. At the growth conditions listed above, $p$-6P molecules form mutually parallel linear aggregates, with width and height of $\sim 200$ and $\sim 100$ nm respectively, and length of several hundred micrometers.
Chapter 3: Self assembled para-sexiphenyl nanofibers

Fig. 3.7. Schematic cross section of Hot Wall Epitaxy system. PHP are the para-hexaphenyl molecules.

3.3. The process of nanofiber self-assembling probed by atomic force microscopy.

The formation process of \( p-6P \) nanofibers has been studied by investigating the morphology of films prepared by HWE with different deposition times. Surface topography has been determined by atomic force microscopy (AFM) [59]. Figure 3.8 shows the AFM surface morphology of \( p-6P \) films on mica substrates, prepared with increasing growth time in the range from 10 sec to 120 min and with a surface temperature of 400 K. As depicted in Figure 3.8 (a), only small uniformly distributed islands can be detected for the sample grown with deposition time of 10 seconds. Increasing the growth time up to 25 sec, the surface morphology changes drastically. When a critical density of islands is reached, a rearrangement of islands occurs resulting in self-organized nanofibers with micrometer length (Figure 3.8 b). As shown in Figure 3.8 b-f, with a further increase of deposition time, these fibers become progressively longer, quickly reaching a fixed asymptotic width [58]. At least after 5 min of growth, nearly no small island could be found on the surface (Figure 3.8 d), while the fibers become closer to each other.
Fig. 3.8. AFM topography images of the p-6P films grown on mica substrates with a deposition time of: a) 10 sec; b) 25 sec; c) 90 sec; d) 5 min; e) 40 min; f) 120 min. Substrate temperature was 400 K. Z-scale is 0-50 nm in (a)-(c), 0-100 nm in (d), 0-220 nm in (e) and 0-700 nm in (f) [59].

Figure 3.9 shows a high resolution 3D-AFM image of a single p-6P nanofiber surrounded by small p-6P islands in the most interesting intermediate growth stage, where islands and fibers coexist. The image clearly reveals that the roughly 850 nm long, 15 nm high and 75 nm wide fiber is not homogenous and consists of about 15 small blocks with approximately the same size as free standing p-6P islands. This result indicates that self-organized fibers on mica are formed by regrouping of mobile individual islands/crystallites originating in earlier growth stages. This thesis is well supported by the observation (using dark-field electron microscopy) of different crystalline p-6P domains within long p-6P nanofibers [60]. As evident from Figures 3.8 b-f, from the very beginning all needles are strictly parallel to each other, having the same preferential orientation relative to the substrate.

The nucleation process described above is made on p-6P films grown by HWE. Analogue results have been found for samples prepared with OMBE so we can conclude that the mechanism of p-6P nanofibers formation based on the nucleation process has general validity.
3.4. Dipole-assisted quasi-epitaxial growth

The \( p \)-6P nanostructure formation and the alignment processes are not fully understood yet. Recent works have been shown that quasi-epitaxial growth mediated by dipole induced-dipole interaction is probably responsible for the growth of the \( p \)-6P nanofibers on polar surfaces such as that of cleaved muscovite mica.

Muscovite mica (\( K_2Al_4[Si_6Al_2O_{20}](OH)_4 \)) is a sheet silicate, consisting of octahedral Al-O layers sandwiched between two tetrahedral Si-O layers [61], as shown in Figure 3.10. In the
tetrahedron layers 1/4 of the Si$^{4+}$ cations are replaced by an Al$^{3+}$. The negatively charged layer packages Al$_2$(OH)$_2$[AlSi$_3$O$_10$] are held together by layers of K$^+$ cations. Cleavage occurs along these interlayer cations (each cleavage face with half of the K$^+$ ions), which is identical with the crystallographic (001) plane of muscovite mica.

The mica unit cell is monoclinic with lattice constants of $a = 5.20$ Å, $b = 9.03$ Å, $c = 20.11$ Å, and monoclinic angle of $\beta = 95.78^\circ$. Transmission electron diffraction and X-ray diffraction studies revealed that there are three epitaxial relations between the $p$-6P crystal in the $\beta$-structure and the mica (001) plane: $(11-1)_{p-6P} \parallel (001)_{\text{mica}}$ and $[1-2-1]_{p-6P} \parallel [-340]_{\text{mica}}$; $(1-11)_{p-6P} \parallel (001)_{\text{mica}}$ and $[-110]_{p-6P} \parallel [-340]_{\text{mica}}$; $(11-2)_{p-6P} \parallel (001)_{\text{mica}}$ and $[-20-1]_{p-6P} \parallel [-310]_{\text{mica}}$ [59,60].

![Fig. 3.11. (a) and (b): Arrangement of $p$-6P molecules in a view parallel to the crystallographic (001) of mica. Panel (a) display a side view while panel (b) a parallel view along the molecular plane. (c): Idealized hexagonal mica surface with contact point lattice, represented by filled circles, of the $p$-6P molecules in the $\beta$-structure. The dashed line indicates the growth direction of the needles [62].](image)

Figures 3.11 (a) and (b) display the relative molecule arrangement of $p$-6P with respect to the mica (001) surface for the first epitaxial relation. The alignment of the molecules is obtained by taking the (11-1) plane of $p$-6P crystal parallel to the mica surface. In all three cases, the alignment of $p$-6P molecules relative to the substrate and to each other is approximately the same. The long molecular axes are not exactly parallel to the mica surface but they are tilted about 4.5° with respect to the mica (001) plane. Therefore, a single $p$-6P molecule contacts the mica surface only at a single point. The distances between the contact points are 26.34 Å and 9.82 Å in the side and in the parallel view, respectively. The molecular planes of adjacent molecules are tilted about 66° relative to each other, generating the typical herringbone structure of the $p$-6P crystal. The interface between the mica (001) surface and the (11-1) plane of $p$-6P are shown in Figure 3.11 (c). The contact points of $p$-6P molecules are indicated by filled
circles, whereas the hexagons represent the idealized mica (001) surface [62]. The periodic contact points between $p$-$6P$ molecules and the mica surface form a two dimensional lattice matched with the correctly oriented mica substrate. This contact point lattice is however incommensurable with the mica (001) lattice; therefore, a quasi-epitaxial growth of $p$-$6P$ on mica (001) lattice is concluded [10]. However, in literature this molecular quasi-epitaxy is called “epitaxial growth”, so in the course of the thesis we refer to it as an epitaxial growth. Since X-ray diffraction experiments give only information about the bulk structure of $p$-$6P$, nothing is known about the arrangement of the molecules within the first monolayer on the mica (001) surface. Transmission electron microscopy in conjunction with transmission electron diffraction measurements showed that the needles grow nearly perpendicular to the long molecular axis of $p$-$6P$ molecules [63]. The dashed arrow in Figure 3.11 (c) represents the growth direction of the fibers.

The epitaxial growth of the $p$-$6P$ fibers is determined by the intermolecular interactions between the $p$-$6P$ molecules as well as the interaction with the substrate surface. Upon cleavage, half of the potassium ions of the mica (001) plane are removed from the surface. The remaining half-monolayer of $K^+$, plus the equal number of substitutional aluminum ($Al^{3+}$) ions, form surface dipoles. The orientation of these dipoles on mica determines the orientation of the molecules on the surface. Since the average dipole moment of the $p$-$6P$ oligomers on the surface is zero, the confinement of the individual molecules to the surface dipoles is most likely due to a dipole induced-dipole interaction. The dipole field on the mica surface is of the order of $10^7$ V/cm [64]. The $p$-$6P$ molecules grow parallel to this field since the interaction energy between the surface dipole and the polarizable molecule is larger than the thermal energy of the molecules. Hence, the interaction between surface dipoles and induced-dipoles along the long molecular axis of the $p$-$6P$ molecules leads to a lying parallel alignment during the initial phase of the growth process.

Once the $p$-$6P$ molecules are oriented in the mica (001) plane, the intermolecular interactions between them cause the formation of the $p$-$6P$ crystal $\beta$-structure. On the other hand, the interaction of the molecules with the single crystalline surface of mica yields to an epitaxial alignment of the $p$-$6P$ crystallites. The epitaxial growth takes place in an islands mode or in a layer-plus-islands mode, as confirmed by the AFM measurements shown above (Figures 3.8 and 3.9). Probably, the anisotropic elastic strain induced by the lattice mismatch between the mica substrate and the first $p$-$6P$ monolayer causes the formation of the crystalline $p$-$6P$ elongated islands in the first stages of the growth [10,14].

Cleavage leads to the formation of terraces on the mica surface, separated by big cleavage steps. In each of these domains, the $p$-$6P$ needles grow parallel to each other, but, from one
domain to another, the orientation of the fibers can be twisted around $120^\circ$. Figure 3.12 shows an epifluorescence micrograph of emitting $p$-6P nanofibers on mica. The step is a clear border which separates areas with different needles orientation. The alignment of the $p$-6P fibers, which is clarified by the two white arrows, is rotated by an angle of $120^\circ$ between the domains. Only two different domains of needles exist on the muscovite mica. LEED and optical microscope measurements reveal that the fibers are oriented along the [110] and [1-10] high symmetry directions of the (001) plane of muscovite mica [65]. No needles grow along the third high symmetry direction [100] (Figure 3.12).

Fig. 3.12. Epifluorescence micrograph of emitting $p$-6P nanofibers grown on two different domains of the muscovite mica. The needles orientations in the two domains, clarified by the two white arrows, form an angle of around $120^\circ$. The white lines on the right indicate the three high symmetry directions [110], [1-10] and [100] on the muscovite mica (001) plane. The $p$-6P fibers are always oriented along the first two directions and never along the [001] direction.

To explain this behavior, we have to consider that muscovite mica is dioctahedral mica, i.e. the inward directed corners of the tetrahedral silicate layers occupy only six of the eight position of each octahedron (see Figure 3.10), the two remain positions being occupied by OH$^-$ anions. This leads to a tilt of the silicon oxide tetrahedron. Cleavage of mica can generate two distinct cleavage planes in which this distortion leads to the formation of grooves along [1-10] and [110] directions [62]. These grooves alternate by an angle of $120^\circ$ between consecutive cleavage layers. Experimentally, the grooves have been observed by atomic force microscopy [66]. This distortion of the mica surface structure probably generates surface electric dipoles nearly perpendicular to the direction of these grooves. No correlation between the surface dipole fields and the anisotropy of the mica cleavage planes has been found yet. However, the existence of surface dipole fields, pointing about $15^\circ$ off the perpendicular to the high symmetry direction,
has been postulated from LEED measurements on freshly cleaved muscovite mica [64]. Therefore, the existence of this electric dipole field nearly perpendicular to two of the high symmetry direction in different cleavage planes, can explain the existence of two distinct domains with different needles orientation.

In conclusion, the \( p-6P \) growth along the [1-10] and [110] high symmetry directions of (001) mica plane, is probably due to a dipole-assisted epitaxial alignment. From epitaxial point of view it is favorable that the molecules are oriented perpendicular to one of the high symmetry direction; this alone would give three equivalent growth directions. However, either [1-10] or [110] is favored because of the orientation of the electric surface dipoles nearly perpendicularly to them [65].

![Fluorescence microscope image (a) and 20 × 20 \( \mu m^2 \) AFM topographic micrograph (b) of \( p-6P \) needles on cleaved phlogopite mica (film grown at a substrate temperature of 440K) [65].](image)

This explanation is supported by the analysis of the \( p-6P \) film grown on a different kind of mica substrate: the trioctahedral phlogopite mica. It has almost the same structure as muscovite mica, but the corners of the tetrahedral silicate layers occupy all the eight position of each octahedron. In phlogopite mica no distortion, and hence no grooves, take place, so only one cleavage plane exists and the three high symmetry directions \([110], [1-10] \) and \([100] \) are equivalent. In cleaved phlogopite mica no large domains with different \( p-6P \) needles orientation has been observed [65]. Fluorescence microscope image and AFM topographic micrograph of 4 nm \( p-6P \) film deposited on phlogopite mica (Figure 3.13. a and b) show very short needles grown along all three high symmetry directions.

The surface structure of cleaved mica, and therefore the surface dipoles strength and orientation, can be changed by treating the cleavage surface before the deposition of organic molecules. For instance, rinsing cleaved muscovite mica in methanol or spraying it with deionized water leads to the replacement of the potassium cations with hydrogen atoms on the
Light amplification in organic self-assembled nanoaggregates

(001) surface [17]. The deposition by BME of organic molecules like oligothiophenes and oligophenyls on substrates which have been treated by methanol or water does not lead to the growth of mutually parallel oriented fibers as in freshly cleaved mica, but results in the formation of micrometer-sized rings and bent fibers [67]. Figure 3.14 shows a collection of fluorescence microscope images (each 20 × 20 µm²) of para-quaterphenyl (p-4P), para-sexiphenyl (p-6P), alpha-quaterthiophene (α-4T) and alpha-sexithiophene (α-6T) deposited on treated mica substrates. Optically active and micrometer or sub-micrometer scaled ring structures can be interesting in resonator amplifier or as integrated elements in more complex photonic circuits [68].

Fig. 3.14. 20 ×20 µm² fluorescence microscope images of p-4P, p-6P, α-4T and α-6T ring-shaped nanostructures on treated mica substrate [67].

3.5. Optical properties of self-assembled p-6P nanofibers

As shown in the previous section, when deposition of para-sexiphenyl and other conjugated oligomers occurs on substrates exhibiting large surface electric dipoles, dipole induced-dipole interaction can lead to the self-assembly of molecular aggregates with submicrometric cross-sectional dimensions, truly macroscopic lengths (up to 1 mm) and high degree of crystallinity. Such a supramolecular order has a big influence on the optical properties of the p-6P films.

3.5.1. Optical anisotropy

The preferential orientation of the molecules on the substrate and the orientation of the needles parallel to each other, lead to a macroscopic anisotropy of the optical absorption and emission [14].

Figure 3.15 (a) depicts the typical polarized absorption spectra of a HWE-grown p-6P nanofibers, parallel oriented on cleaved muscovite mica substrate, for different angles of the polarizer with respect to the fibers axis. The plotted curves show a well-pronounced maximum around 366 nm for the polarization perpendicular to the needles (90°), while, for polarization parallel to the needles (0°), no significant absorption bands can be observed. At 366 nm the
dicroic absorption ratio between the parallel and perpendicular polarization is more than 11 dB. The 366 nm absorption band is attributed to the $\pi-\pi^*$ dipole transition of the $p$-6P molecules.

Figure 3.15 (b) shows the typical photoluminescence spectra of $p$-6P nanofibers film taken at two polarization geometries (inset of Figure) with respect to the nanofiber orientation. The maximum of emission is observed again for excitation and collection polarization perpendicular to the needle axis. The dicroic ratio for $90^\circ-90^\circ$ emission compared to $0^\circ-0^\circ$ is $\approx 14$ dB.

![Figure 3.15](image)

**Fig. 3.15.** (a): Angularly resolved polarized absorption spectra of $p$-6P film at normal incidence; $0^\circ$ and $90^\circ$ relates to the field parallel and perpendicular to the needles direction, respectively. (b): Polarized photoluminescence spectra of $p$-6P film for excitation at 350 nm. The inset shows a schematic representation of measuring geometries [14].

### 3.5.2. Optical waveguiding

Cross-sectional dimensions (~ 100 nm in high and ~ 300 nm in width) of $p$-6P nanofibers enable single-mode optical waveguiding of the visible light. Linear waveguiding near 425nm, at the 0-1 vibronic band of the emission spectra of $p$-6P has been demonstrated recently [56,69]. Analytical theory for optical waveguiding in nanometer-scaled dielectric nanoaggregates allows to calculate the propagation constant and the cut-off wavelength for the guided modes.

Mathematically, the propagation of the electric and magnetic fields in a dielectric medium having a dielectric tensor $\hat{\varepsilon}$ and magnetic permeability $\mu$ is described by the Helmholtz wave equations [70]:

$$\left( \nabla^2 + \frac{\omega^2}{c^2} \hat{\varepsilon} \right) \begin{pmatrix} E \\ B \end{pmatrix} = 0$$

The determination of the propagating modes in a dielectric waveguide requires solving these equations with appropriate boundary conditions.
In the case of $p$-$6P$ nanofiber, the waveguide can be approximated by a rectangular waveguide with side $a$ and $b$ on a dielectric substrate (Figure 3.16).

![Fig. 3.16. Rectangular approximation of the $p$-$6P$ needle as dielectric waveguide model.](image)

The dielectric constants of the medium surrounding the waveguide and of the substrate are $\varepsilon_1$ and $\varepsilon_3$ respectively ($\varepsilon_2 = 1 < \varepsilon_3$). The waveguide is taken optically uniaxial with dielectric permittivity tensor:

$$\hat{\varepsilon}_2 = \begin{pmatrix} \varepsilon_{||} & 0 & 0 \\ 0 & \varepsilon_{\perp} & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{pmatrix}$$

where $\varepsilon_{||}$ and $\varepsilon_{\perp}$ are the components of the dielectric tensor in the direction parallel and perpendicular to the long molecular axis, respectively. The imaginary part of $\varepsilon_{||}$ and $\varepsilon_{\perp}$ are much less than their real part and $\varepsilon_{||} > \varepsilon_{\perp}$. The magnetic permeability $\mu$ is taken $= 1$ in all three media. The solution of Helmholtz equations, for electric and magnetic field propagating in the $z$ direction, are of the form:

$$E_{\alpha j}(x, y, z) = E_{\alpha j}^0(x, y)e^{i(\omega t - \beta z)}$$

$$H_{\alpha j}(x, y, z) = H_{\alpha j}^0(x, y)e^{i(\omega t - \beta z)}$$

where the suffix $\alpha$ indicate the three direction $x, y, z$, $j = 1, 2, 3$ refers to the three medium, and $\beta$ is the (modal) propagation constant. Imposing the boundary conditions requiring the continuity of the components along $x$ and $y$ of the electric and magnetic fields between the three media, it has been demonstrated [56] that the nanofiber waveguide model can support the propagation of transverse magnetic (TM) modes whereas the transverse electric (TE) mode cannot exist. The TM propagation constant within this model can be written as:
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\[
\beta = \left[ \frac{\omega^2}{c^2 \varepsilon_{ij}} - \frac{\varepsilon_{ij}}{\varepsilon_\perp} \left( \frac{m\pi}{a} \right)^2 \right]^{1/2} \quad \text{with } m=1,2,3,...
\]

From this equation we can find that the (TM) waves frequency has to be \( \omega > \frac{c}{\sqrt{\varepsilon_\perp}} \frac{m\pi}{a} \).

Therefore, the cutoff wavelength is:

\[
\lambda_c(m) = \frac{2a \sqrt{\varepsilon_\perp}}{m}.
\]

The number of possible modes, \( m=1, 2, 3,.., \) is restricted by the condition \( m < \frac{2a}{\lambda} \sqrt{\frac{\varepsilon_\parallel}{\varepsilon_{ij}}} \sqrt{\varepsilon_\parallel - \varepsilon_\perp} \).

If we take \( \varepsilon_\parallel = 1 \), the mica refractive index \( \sqrt{\varepsilon_3} = 1.58 \) and the value for an isotropic para-sexiphenyl film \( \sqrt{\varepsilon_3} = 1.7 \) at \( \lambda = 425\text{nm} \), we obtain \( \varepsilon_\parallel = 4.8 \) and \( \varepsilon_\perp = 1.9 \) [56]. Using these values, we can estimate that the minimum fiber width \( (a_{\text{min}}) \) for which at least one mode at 0-1 band of the \( p-6P \) emission spectra \( (\lambda = 425\text{nm}) \) can propagate in the nanofiber is equal to 222 nm.

The imaginary part of the propagation constant \( \beta \) gives the losses of the propagating light due to the material reabsorption:

\[
\alpha = \frac{2\pi \varepsilon_\perp}{\lambda \sqrt{\varepsilon_\parallel}} \left[ 1 - \frac{1}{\varepsilon_\perp} \left( \frac{\lambda}{2a} \right)^2 \right]^{1/2}
\]

where \( \varepsilon_\parallel \) and \( \varepsilon_\perp \) are the real and imaginary part of the component of dielectric tensor parallel to the long molecular axis, and \( \lambda \) is the wavelength in vacuum of the guided mode. The imaginary part of the component perpendicular to the long molecular axis is supposed negligible [71].

In a real \( p-6P \) nanofiber waveguide the losses of the confined modes are due to the material reabsorption and to light scattering. The total propagation losses for the waveguided mode at 425 nm can be estimated experimentally. Balzer et al. [56], exciting locally an isolated nanofiber, measured the outcoupled luminescence intensity from a fiber break at a variable distance between the excitation and outcoupled point (Figure 3.17). The intensity of the waveguided light decreases exponentially with the distance along the waveguide \( (I(z)) = I(z_0) e^{-\alpha(z-z_0)} \), where \( \alpha = \text{Im} \beta \), so from the experimental measurements of outcoupled luminescence intensity as a function of distance from excitation point, it could be estimated that the total propagation losses in \( p-6P \) nanofiber are \( \alpha \sim 100$–$300 \text{ cm}^{-1} \), depending on the selected nanofiber.
Fig. 3.17. (a): Fluorescence images of emitting individual p-6P nanofiber (width $a \approx 400\text{nm}$), taken at five different distances between excitation and outcoupling point. (b): Outcoupled luminescence intensity as a function of distance from the excitation point. The red line is a fit to the experimental data. The dashed line represents the spatial excitation profile [56].

The analytical model for optical waveguiding in rectangular nanoaggregates allows also to estimate the confinement factor of the waveguided mode, defined as the ratio of the light intensity within the nanofiber to the sum of light intensity both within and outside the guide:

$$
\Gamma = \Gamma_{xy} = \frac{\int_{0}^{h} \int_{0}^{w} |E(x,y)|^2 \, dx \, dy}{\iint \int |E(x,y)|^2 \, dx \, dy}
$$

The confinement factor of p-6P nanofibers, at the wavelength of 425 nm, has been estimated to be $\sim 0.9\%$ for fiber height and width of 90 and 220 nm respectively, and $\sim 1.2\%$ for height and width of 120 and 220 nm [72].
CHAPTER 4

EXPERIMENTAL METHODS

Different experimental techniques have been used in this work to characterize the samples of $p$-6P self-assembled nanofibers. For a morphological study we used an atomic force microscope (AFM) in “tapping mode” configuration, particularly suitable to investigate soft samples like those of our interest. The optical emission properties have been studied using standard spectroscopic techniques like spectrally- and spatially-resolved photoluminescence and lasing measurements.
4.1. Atomic Force Microscopy

Atomic force microscope is one of the family of scanning probe microscopes in which a sharp probe is scanned across the surface of the sample and some sample-probe interactions measurement allows a study of the surface topography, theoretically with atomic resolution in all directions in space.

The sensitive element (probe) in the AFM is an elastic cantilever, usually made on silicon or silicon nitride, in the free end of which a sharp tip is fabricated (fig. 4.1).

![Fig. 4.1. Schematic representation of the principle of working of the AFM.](image)

When the tip is brought close to the sample surface the interatomic forces between the tip and the sample cause a bending of the cantilever. This deflection is measured optically detecting the variations in the direction of a laser beam reflected from the cantilever. As the tip is scanned over the sample surface, it allows to map out its topography.

The resolution of the AFM depends mainly on the sharpness of the tip, which can be manufactured with an end radius of few nanometers. Atomic resolution can be obtained only with relatively robust and periodic samples, in contact mode.

With soft samples as organic materials however, is more difficult to image the surface because the forces exerted by the tip during the scanning can cause deformations and damages in the sample. This problem has been overcome by using the AFM in tapping mode. In this operating mode, the cantilever oscillates in a direction perpendicular to the surface, resulting in only intermittent contact between the tip and the surface. This greatly reduces the lateral forces that are responsible for most of the damage of the samples as the tip is scanned. Figure 4.2 shows a schematic representation of the tapping mode AFM.
Chapter 4: Experimental methods

Fig. 4.2. Simplified representation of the AFM operating in tapping mode.

The cantilever oscillates at or near its resonance frequency with amplitude ranging typically from 20nm to 100nm. The feedback loop maintains constant oscillating amplitude by maintaining a constant RMS of the oscillating signal acquired by the split photodiode detector (fig.4.2). The vertical position of the scanner for each x-y position in order to maintain a constant set point amplitude is stored by the computer to form the topographic image of the sample surface. Tapping mode AFM is capable of better than 1 nm resolution on ideal samples.

In this work, a standard AFM “SolverPRO” manufactured by NT-MDT has been used. The instrument has two different scanning modes: scanning by probe, in which the probe moves across the surface of a stationary sample, and scanning by a sample which moves relative to the probe. In all the measurements on p-6P samples shown in this thesis, scanning by probe operating mode has been used. Silicon rectangular cantilevers with typical thickness of 2.0 µm and resonance frequency between 115 and 190 KHz has been employed. The probe tips have a height of 10-15 µm and a typical curvature radius of 10 nm.
4.2. Spectrally- and spatially-resolved photoluminescence

In this work, two different experimental setups have been used to study the emission properties of the \( p \)-6P nanofibers. The first setup, shown in Figure 4.3, has been used to study the luminescence and lasing emission of photoexcited samples with high density of nanofibers.

Fig. 4.3. Schematic representation of luminescence setup. RGA: regenerative amplifier laser system; M: mirrors; m: movable mirrors; L: achromatic lenses; \( F_1 \): coloured filter BG38; \( F_2 \): coloured glass filters GG400; \( F_{ND} \): neutral density variable filters; \( \lambda/2 \): half wave plate.

Fig. 4.4. Different excitation and collection geometries in the luminescence setup.
In this experimental setup, the excitation source is a Ti:sapphire regenerative amplifier (RGA) delivering 150 fs laser pulses at wavelength of 780 nm, repetition rate of 1 KHz and energy 1 mJ per pulse. To excite the samples in their spectral absorption region, we generate the second harmonic of the RGA output with a 2 mm thick BBO crystal. A set of calibrated neutral density filters (F_{ND}) is used to study the emission spectrum of the samples at different excitation density in order to determine the lasing threshold. A half wave plate (λ/2) allows us to set the polarization of the laser pulses parallel to the long molecular axis of p-6P molecules so that a maximum material absorption can be achieved. The laser beam is then focalized by 120cm lens in the sample surface giving an excitation spot diameter of ~120µm. The samples are mounted in a recirculating-loop cold-finger cryostat for low temperature measurements (from 30 K to room temperature). The samples can be rotated so that measurements in different excitation and collection configurations can be made. The samples can be excited at normal incidence or at different angles and the emission can be collected in transmission, at the edge or in reflection (fig. 3.4).

The emission of the sample, suitably filtered from the remaining excitation laser beam, is collected by a optical system with an f-number (F/#) of 4 and dispersed in a 46 cm single spectrometer. The detection system is a LN_{2} cooled silicon CCD. The spectral resolution achievable with the system is 2Å. A CCD camera and a white light lamp allow us to select the proper domains of the samples surface where to make the measurements and the proper nanofibers orientation.

The second experimental setup, shown in Figure 4.5, has been used to resolve spatially and spectrally the photoluminescence and the lasing emission of samples with single isolated nanofibers. The setup is almost the same shown in Figure 3.4 except that in the last we used a microscope objective with 32x magnification and 0.40 numerical aperture to collect the emission of the samples and to focus it in the plane of the entrance slit of the spectrometer.
Light amplification in organic self-assembled nanoaggregates

Fig. 4.5. Schematic representation of experimental setup for spectrally- and spatially- resolved photoluminescence. RGA: regenerative amplifier laser system; M: mirrors; m: movable mirrors; L: achromatic lenses; F₁: coloured filter BG38; F₂: coloured glass filters GG400; F₁ND: neutral density variable filters; λ/2: half wave plate; D: iris diaphragms.

The setup has been used in two different configurations. Setting the grating to the zero order diffraction the system, equipped with a two dimensional detector (a LN₂ cooled CCD), can be used as an imager (spatial mode configuration). The spatial resolution achievable with the system, checked by using a calibrated test target, is ~ 2 μm. Figure 4.6 (a) displays, as an example, an image of a sample region with isolated nanofibers and the emission profiles in both the x and y directions. Accounting for the 32x magnification and the pixel dimension of the CCD (26×26μm²), a region of the sample of a ~ 65 (horizontal) × 200 (vertical) μm², within the excitation spot, can be imaged with the input slit fully opened (2mm).

1

Setting the grating of the spectrometer to the first order diffraction and closing the input slit at 100μm it is possible to select spatially, with the same resolution (2μm), the emission of a single isolated nanofiber aligned parallel to the entrance slit and resolve it spectrally with a resolution of about 0.2 nm (spectral mode configuration). As an example of this operating mode, Figure 4.6 (b) shows the emission intensity of the selected nanofiber, which appears in the centre of the image in Figure 4.6 (a). The emission is spectrally resolved in X direction and spatially resolved in Y.
Fig. 4.6. (a) Gray scale emission intensity image of a sample region with sparse p-6P nanofibers with the profiles of the emission intensity in X (top) and Y (right) directions. (b) Gray scale emission intensity image, spectrally resolved in the X dimension and spatially in Y, of the central fiber shown in panel (a); emission spectrum of the fiber taken in the region Y=115-125 pixels (top) and spectrally integrated emission profile (right) are shown.
CHAPTER 5

RANDOM LASING
AND OPTICAL GAIN
IN p-6P NANOFIBERS

In this chapter, we present an investigation on the morphology and emission properties of p-6P needle-shaped aggregates grown on muscovite mica substrate. The nanoaggregates topography is probed by atomic force microscopy. Spontaneous and stimulated light emission, as well as laser action, is investigated through the micro-spectrographic system showed in chapter four, providing both spectral and spatial resolution. Correlations between morphology and stimulated emission properties are pointed out. The first part of this section is dedicated to the properties of samples with close-packed nanofibers having different widths and heights, both in ensemble-averaged and spatially-resolved measurements. In the second part, we analyze lasing and amplified spontaneous emission (ASE) properties in isolated p-6P nanofibers. We present some theoretical models to quantitatively support the interpretation of experimental results. We assess basic material parameters like the net optical gain coefficient and the stimulated emission cross-section.
5.1. Light amplification in close-packed $p$-6P nanofibers

5.1.1. Random lasing

Samples shown in this section are grown by the group of professor H. Sitter, (University of Linz, Austria), by Hot Wall Epitaxy.

The first sample shown is a $p$-6P film grown on freshly cleaved muscovite mica substrate at a temperature of 400 K, with evaporation time of 40 minutes. Figure 5.1 (a) shows a tapping mode AFM topographic image of a $10\times10$ µm$^2$ region of the sample.

Fig. 5.1. (a): AFM topography image of a $10\times10$ µm$^2$ region of a $p$-6P film on mica; z scale is 0-220 nm. (b): Experimental fiber height distribution. (c): Experimental fiber width distribution. Red lines are the corresponding Gaussian fits to the data.

Almost all the nanofibers are oriented in the same direction and are close-packed. They cover a sample surface region of about 50 %, and have a length of several hundred micrometers. The height and width distributions are measured from the AFM image with a line profile along the direction perpendicular to the needle axis. The results are shown in Figure 5.1 (b) and (c), with the corresponding Gaussian fit to the experimental data. The average fiber height and width is 110 and 220 nm, respectively [59]. Theoretical models show that the nanofibers can support light propagation at 425 nm only if their width is larger than 220 nm (see § 3.5.2). Therefore only the needles lying in the upper side of the width distribution can contribute to amplification of spontaneous emission and laser action at the 0-1 vibronic peak (425 nm) of the emission spectra of $p$-6P.
Optical emission properties of this sample are studied with both ensemble-averaged and spatially-resolved photoluminescence measurements (§ 5.1.3).

The ensemble-averaged results, taken using the photoluminescence setup shown in Figure 4.3, are analyzed first. The sample is excited at normal incidence and the excitation spot size, having a diameter of 120 µm, allows to pump a large number of nanofibers. Figure 5.2 shows a series of spectrally resolved emission measurements, taken at the temperature of 30 K, for different excitation energy densities $\Phi$, and collected normally to the sample surface.

![Emission Spectra](image)

**Fig. 5.2.** Emission spectra, taken at the temperature of 30 K, for different values of pump fluence $\Phi$ (µJ/cm$^2$ per pulse).

At low excitation fluence, spontaneous emission exhibits the typical vibronic progression of p-6P, with 0-1 and 0-2 bands centered at 425 and 450 nm, respectively. When the excitation fluence reaches a threshold value ($\Phi_{th}$) of about 0.5 µJ/cm$^2$ per pulse, very narrow and randomly spatially distributed spectral lines suddenly emerge from the spontaneous emission spectrum at the 0-1 vibronic peak. The lines have a resolution-limited width of 0.2 nm.

The emission is found to be highly polarized, with a polarization ratio larger than 7 dB across the entire spectral emission range, as it can be seen in Figure 5.3. This is due to the high crystal order of the nanofibers and to the anisotropic distribution of the fibers in the sample surface (Figure 5.1).
Light amplification in organic self-assembled nanoaggregates

Fig. 5.3. Emission spectra measured after polarization filtering along the direction parallel (//) and perpendicular (⊥) to the long molecular axis of p-6P. Blue dots: Intensity ratio between the two polarizations.

The spectral distribution of the narrow lines is strongly dependent on the sample excitation region. Figure 5.4 shows the emission measured in two different regions of the sample surface at the same excitation fluence. In these data, the contribution of the spontaneous emission has been subtracted in order to highlight the laser-like response in the spectral pattern above threshold. The spectral shape of the emission does not change when repeating the measurements in the same region at different times, so we can exclude that the narrow lines are experimental artifacts.

Fig. 5.4. Emission spectra measured in two different sites of the sample surface at the temperature of 300 K.

The threshold pump fluence $\Phi_{th}$ also depends strongly on the sample excitation region (we measured variations up to a factor of ten) but is independent on the temperature in the range between 30 K and 300 K, within our experimental accuracy of 10%. The lowest value of the
Chapter 5: Random lasing and optical gain in p-6P nanofibers

threshold fluence measured in this sample is $0.5 \mu J/cm^2$ per pulse. Being the material absorption of about 30%, the covered area of the sample surface ≈ 50%, and assuming that the conversion efficiency of the absorbed pump energy into singlet excitons is equal to 100%, for $\Phi_{th} = 0.5 \mu J/cm^2$ we estimate the lowest threshold density $N_{th} \approx 6 \times 10^{16} cm^{-3}$.

All these emission characteristics are reproduced in the temperature range between 30 K to 300 K and using collecting optics with different numerical aperture and different excitation and collection geometries.

The observed phenomenology can be attributed to coherent random lasing, arising from recurrent scattering along the nanofibers [73]. The optical feedback necessary for laser action originates from cracks, bends, sudden variation in fiber height and width and intersection points between different fibers. All these inhomogeneities act as scattering centers. The light diffused by a scatterer can come back to the same scatterer after experiencing a sequence of scattering processes in the p-6P film, hence forming a close-loop path for light amplification. Lasing starts when the close loop amplification overcome the losses, provided that the total phase variation in the loop has to be equal to integer multiple of $2\pi$.

Owing to the random phase acquired in each scattering process and to the randomness of the single-path length (between subsequent scattering events), random lasing frequencies are realized. As the pump fluence is increased, a growing number of closed-loop random paths existing within the photoexcited spot reaches threshold, resulting in the appearance of additional discrete peaks in the emission spectrum.

The evolution of the emission spectrum as a function of the excitation power is very similar to that reported in an ensemble of dye-filled microcrystals, where laser oscillation begins on low-optical loss single crystals, while the other microresonators with large losses, contribute to the ensemble response with spontaneous emission only [74]. Coherent random lasing with very similar features has been reported over the last few years in a variety of solid state, high-gain materials, including films of organic molecules like substituted thiophene-based oligomers [33-37].

The interpretation of the non linear emission in p-6P films as coherent random lasing is also supported by the results of spectrally- and time-integrated emission intensity measurements as a function of excess pump fluence, defined as $\frac{\Delta \Phi}{\Phi} = \frac{\Phi - \Phi_{th}}{\Phi_{th}}$. Figure 5.5 shows the experimental data (black dots) with the corresponding fit, plotted on a logarithmic scale. The intensity is integrated over the random lasing spectral region, after subtraction of the contribution of spontaneous emission.
Light amplification in organic self-assembled nanoaggregate

The spectrally integrated intensity increases nearly quadratically with $\Delta \Phi/\Phi_{th}$, and saturation possibly occurs at higher pump levels. This superlinear behavior can be attributed to the inhomogeneity of the ensemble, due to the presence of fibers with different sizes and shape, and exhibiting different optical losses. Therefore when the excitation fluence is increased, the total number of modes that reach the oscillation condition also increase. Consequently the output power depends superlinearly on the pump fluence.

5.1.2. Amplified Spontaneous Emission

In addition to coherent random lasing, as the excitation fluence is increased, optical gain exceeds the losses in an increasing number of open-loop paths, yielding to amplification of spontaneous emission (ASE or incoherent random lasing). Spectral narrowing due to the ASE process is evident in the Figure 5.6, where the emission spectra as a function of the pump fluence, at high excitation density, have been plotted. ASE is also evident at the 0-2 vibronic band of $p$-6P, near 450nm. The occurrence of an ASE process in high-losses nanofibers explains also the persistence of superlinear growth of the spectrally integrated emission intensity shown in Figure 5.5, and the progressive decrease in visibility of random lasing modes at large values of excitation fluence (fig. 5.6) [36].

![Graph showing SI Intensity vs normalized pump excess fluence](image-url)
Fig. 5.6. Emission spectra taken at different values of excitation fluence $\Phi$ ($\mu$J/cm$^2$ per pulse), at the temperature of 300 K, on the sample shown in Figure 5.1.

5.1.3. Spatially-resolved lasing emission

To have a deeper understanding of the random lasing origin in p-6P nanofibers films, spatially- and spectrally-resolved measurements on the sample shown in Figure 5.1 have been performed.

Fig. 5.7. Gray scale image of spatially resolved nanofibers emission above random lasing threshold. The white markers delimit the area over which the spectrally resolved emission shown in fig. 5.8 is spatially integrated.
Using the luminescence set-up explained in chapter 4 (fig. 4.5), and a laser spot of 180 µm in diameter, a surface region in the edge of a domain where the nanofibers are sparse, has been excited. Figure 5.7 shows a gray scale micrograph of a sample region smaller than the excitation spot, taken at excitation fluence above random lasing threshold, so that it displays both spontaneous and coherent emission. It can be distinguished the emission from single partially isolated nanofibers, which however are optically interconnected.

The emission spectra are measured integrating over the small 3×56 µm² area indicated by the white markers in Figure 5.7. In this way, the emission of a single nanofiber segment has been selected. Figure 5.8 show the spectra for different pump fluences below and above lasing threshold, for this selected segment.

![Emission spectra](image)

**Fig. 5.8.** Emission spectra taken at different values of excitation fluence Φ (µJ/cm² per pulse), at the temperature of 300 K, and integrated over the region delimited by the white markers in Figure 5.7.

The results are similar to those observed in ensemble-average measurements shown previously: discrete random lasing peaks emerge from the emission spectrum at the 0-1 vibronic band of p-6P, near 425nm, when the excitation fluence reaches a threshold value. Lasing is observed also at the 0-2 vibronic peak near 450nm.

The strong similarities between the ensemble-averaged spectra and the spatially-resolved spectra suggest that in these nanofibers coherent random lasing has a one-dimensional character. Thin cracks and other sites, where sudden variation in fiber thickness or width occurs, can explain the build-up of one-dimensional random optical cavities in individual nanofibers. In this sample, however, there are no fully isolated nanofibers but only isolated segments which can be
resolved spectroscopically. It is possible that closed-loop random paths extend over many cross-connected nanofibers. In such a limit case, cross-connection points would represent the dominant scattering centers and the resulting random cavities would be merely two-dimensional. This issue will be clarified in the § 5.3.1, where lasing emission measurements in combination with AFM morphological characterization on isolated nanofibers are presented.

5.1.4. Film thickness dependence of optical response

Very similar results are obtained for samples with different growth conditions. Figure 5.9 (a) shows the AFM topography image of a p-6P film grown by Hot Wall Epitaxy on freshly cleaved mica substrate at the same temperature of the sample shown in Figure 5.1 (a) (400 K), but with an evaporation time of 120 minutes.

![AFM image](image)

Fig. 5.9. (a): AFM topography image of a 10×10 µm² region of a p-6P film on mica; z scale is 0-700 nm. (b): Experimental fiber height distribution. (c): Experimental fiber width distributions. Red lines are the Gaussian fits to the data.

In this sample the p-6P nanofibers are more close-packed than in the previous one (Figure 5.9 a), and their mean height and width are 190 nm and 350 nm respectively (Figure 5.9 b and c).

Figure 5.10 displays the spectrally-resolved ensemble emission as a function of the excitation fluence Φ, at ambient temperature. Coherent random modes are less pronounced than in sample of § 5.1.1. Furthermore the threshold pump fluences measured in this sample are higher (from 10 µJ/cm² to 100 µJ/cm² depending on the surface region). These experimental results can be explained with a larger film inhomogeneity that is responsible for an increased efficiency of light scattering into out of plane direction. The possibilities of building-up in-plane closed-loop paths for coherent random lasing are subsequently reduced. However, as in the
previous sample, a spectral narrowing of the 0-1 vibronic band at 425nm due to the ASE process has been found.

![Emission spectra taken at different values of excitation fluence \( \Phi (\mu J/cm^2) \) per pulse, at the temperature of 300 K, on sample with high density of nanofibers (Figure 5.7).]

The AFM image of the third sample analyzed in this section is shown in Figure 5.11 (a). It is a \( p \)-6P film grown by Hot Wall Epitaxy on freshly cleaved mica substrate at the temperature of 400 K with an evaporation time of 5 minutes.

The \( p \)-6P nanofibers are much sparser than in the previous samples, and the mean height and width are 120 nm and 140 nm respectively, as shown in Figure 5.11 (b) and (c). From a statistical analysis based on the data shown in Figure 5.11 (c), the fraction of nanofibers with width larger than 220 nm (that is the cut-off width for waveguiding at 425 nm) has been estimated less than 2%. From the ensemble-averaged measurements, lasing emission has not been detected in this sample for excitation fluence as high as 2 mJ/cm². Lack of laser action can be attributed to poor optical waveguiding due to insufficient fiber width.
Chapter 5: Random lasing and optical gain in p-6P nanofibers

Fig. 5.11. (a): AFM topography image of a 10×10 µm² region of a p-6P film on mica; z scale is 0-100 nm. (b): Experimental fiber height distribution. (c): Experimental fiber width distribution. Red lines are the Gaussian fit to the data.

5.2. Bimolecular singlet-singlet annihilation process in p-6P aggregates

Nonradiative processes as singlet-singlet annihilation, singlet-polaron and singlet-triplet scattering are important source of density-dependent losses in crystalline and amorphous organic films. In particular, in crystalline materials, since the singlet exciton diffusion constant increases with molecular order, these decay channels acquire an important role. Furthermore, the singlet-singlet annihilation process is much stronger in crystalline films than in disordered materials, whereas singlet-polaron and singlet-triplet losses are usually weaker. So the singlet-singlet recombinaton process becomes the dominant nonradiative loss mechanism in these materials [75].

Density-dependent effects are observed in our spectrally- and time-integrated measurements of the spontaneous emission intensity as a function of pump fluence. In Figure 5.12 (a) the integrated intensity has been plotted as function of the estimated excitation density $N_0$, for pump fluence below the threshold of random lasing. The data refer to a region of the sample shown in Figure 5.1 where the threshold density is $N_{\text{th}} = 2×10^{17}$ cm$^{-3}$.
Fig. 5.12. (a): Black solid dots are experimental points of spectrally- and time-integrated emission intensity vs excitation density $N_0$ below threshold at temperature of 30 K; in red is the fit to the experimental data, using equation (5.1). (b): Photoluminescence decay (black line) with its single exponential fit (red line).

The origin of the sub-linear behavior is attributed to the bimolecular single-singlet annihilation process. An estimate of the bimolecular recombination rate $k_{ss}$ has been obtained by the data fitting shown in Figure 5.12 (a).

If the optical excitation pulse-width is short compared to the decay time of the exciton, and neglecting density dependent losses other than bimolecular recombination process, than the rate equation for the excitons recombination can be written as [38].

$$\frac{dN}{dt} = -k_{PL}N - k_{ss}N^2$$

where $N$ is the singlet exciton population density, $k_{PL}$ is the inverse of the observed photoluminescence lifetime at low excitation density and $k_{ss}$ is the bimolecular recombination rate.

The measured time-integrated emission intensity ($S_{TI}$) is proportional to the solution of the rate equation:

$$S_{TI} \propto \int N(t)dt \approx \ln \left( \frac{k_{ss}N_0}{k_{PL} + 1} \right)$$

where $N_0$ is the estimated singlet exciton density at the time of excitation ($t = 0$).

The value of $k_{PL}$ has been measured in a time resolved experiment using a streak camera Hamamatsu C5680 that, in combination with a spectrometer, allows to make spectrally and time resolved measurements with temporal resolution of about 2 ps. The sample is photopumped with excitation fluence $\Phi \approx 0.1$ nJ/cm$^2$ per pulse. The photoluminescence decay is shown in Figure 5.12 (b). The single exponential fit (red line) gives a decay time of 550 ps, from which we find: $k_{PL} = 1.8 \times 10^9$ s$^{-1}$. 

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From the fitting to the spectrally integrated intensity (Figure 5.12 a), using the expression given in the equation (5.1), we find \( k_{ss} = (0.9 \pm 0.2) \times 10^{-7} \text{ cm}^3\text{s}^{-1} \). By comparing data sets obtained in different positions of the sample, we determine that the value of the singlet-singlet annihilation rate \( k_{ss} \) is:

\[
k_{ss} = (0.3 - 1.1) \times 10^{-7} \text{ cm}^3\text{s}^{-1}
\]

This high value of the bimolecular recombination rate can be attributed to the high molecular order of \( p\)-6P nanofibers film, and it is comparable to the value reported in literature for other crystalline films as for example in tetracene single crystals [76].

### 5.3. Light amplification in single \( p\)-6P nanofibers

In the previous section, the results of ensemble-averaged and spatially-resolved measurements on films of close packed \( p\)-6P nanofibers, which optically interact with each other, have been discussed. The observed laser-like emission has been explained in term of random lasing in which the optical feedback necessary for laser action originates from the fiber inhomogeneities.

In order to get a deeper knowledge about the intrinsic emission properties of isolated self-assembled \( p\)-6P nanofibers, we studied different samples in which the \( p\)-6P needles are very sparse. Figure 5.13 shows an epifluorescence image of a 290\times220 \( \mu \text{m}^2 \) region of one of these samples. The micrograph is taken using an inverted microscope Nikon with a cw arc lamp as the excitation source in the spectral range of 330-380 nm. The \( p\)-6P nanofibers appear well isolated and long several hundred micrometers.

![Fig. 5.13. 290\times220 \( \mu \text{m}^2 \) epifluorescence image of isolated \( p\)-6P nanofibers.](image)

The samples shown in this section are grown by the group of Professor H. G. Rubahn (University of Odense, Denmark). The \( p\)-6P molecules are deposited on freshly cleaved
muscovite mica substrate by vacuum sublimation at typical rate of 0.1 Å/s, under a dynamic vacuum of $\approx 2 \times 10^{-7}$ mbar and at substrate temperature of around 420 K.

### 5.3.1. One dimensional random lasing

Figure 5.14 (a) depicts the tapping-mode AFM topographic image of the surface morphology of a $\approx 5 \times 5.5$ µm$^2$ substrate area with sparse $p$-6P nanofibers. Here the typical features of isolated nanofibers in the length scale of a few micrometers can be noticed. The nanofibers have a base width of 300 nm or larger, which enables waveguiding of the spontaneous emission of $p$-6P beyond 400 nm (§ 3.5.2). The small islands lying between adjacent nanofibers are remnants of the nucleation process of $p$-6P into oriented fibers, described in § 3.3.

From Figure 5.14 (a), it can be noticed that the fibers are segmented by the occurrence of cracks, which are typically 50 to 300 nm wide. Such thin brakes occur possibly at the end of material growth process, as a result of surface thermal gradient while the substrate is cooling down [77], or are due to an instability similar to that verified in films of different functionalized molecules deposited on mica substrate [78].

Fig. 5.14. (a): Gray scale AFM topographic image of a 5.5×5.5 µm$^2$ region of $p$-6P nanofibers grown on muscovite mica. Black and white levels correspond to $p$-6P heights of 0 nm and 95 nm, respectively. (b): Epifluorescence image of a 95×70 µm$^2$ region of the same sample of panel (a).

Breaks characterize most nanofibers in the analyzed samples, although it is possible to find regions of the samples with nearly break-free nanofibers. In addition to the material cracks, Figure 5.14 (a) shows that there exist sites of the nanofibers where sudden variations in its width or height occur. These inhomogeneities are also evident in the epifluorescence image shown in Figure 5.14 (b), made on the same sample. Bright spots of scattered luminescence correspond to breaks distributed along the nanofibers, as we will demonstrate in this section by correlated optical and topographic measurements.
Optical emission properties of isolated nanofibers are studied with spatially- and spectrally-resolved measurements, using the set-up described in chapter four (Figure 4.5).

Lasing emission from isolated nanofibers is shown in Figure 5.15. Figure 5.15 (a) shows a micrograph of p-6P nanofibers emission taken with the spectrometer in imaging mode, at excitation fluence slightly above random lasing threshold. It displays both lasing and spontaneous emission from vertically aligned nanofibers and spontaneous emission from a set of neighboring nanofibers oriented approximately at 60 degrees with respect to the vertical axis of the detection system. These latter faintly appear in the lower part of the graph. Scattering of the lasing emission into out-of-plane directions does not take place homogeneously along the nanofibers’ axis; conversely, scattering is highly spotted, indicating that waveguiding is interleaved with light scattering and outcoupled at special sites along the fibers.

Figure 5.15 (b) reports the emission spectrum as a function of the excitation fluence \( \Phi \), relating to the \( \sim 100 \) \( \mu \)m long nanofiber placed at the center of the imaging field of view in Figure 5.15 (a), e.g. positioned at \( X \approx 30 \mu \)m and extending vertically from \( Y \approx 50 \mu \)m to \( Y \approx 150 \mu \)m. The spectra refer to the emission spatially-integrated over the whole nanofiber length.

![Fig. 5.15](image.png)

**Fig. 5.15.** (a): Blue levels scale micrograph of optical emission intensity of lasing luminescent p-6P nanofibers excited at pump fluence \( \Phi = 15 \mu J/cm^2 \) per pulse. (b): Emission spectra of the nanofiber positioned at \( X \approx 30 \mu m \) in panel (a) and extending vertically from \( Y \approx 50 \mu m \) to \( Y \approx 150 \mu m \), for different values of excitation fluence.

Below threshold, spontaneous emission exhibits a broad vibronic progression with 0-1 and 0-2 emission bands peaked near 425 nm and 450 nm, respectively. When the excitation fluence
reach a threshold value of about 10 µJ/cm² per pulse (depending on the selected nanofibers), very narrow peaks (resolution-limited spectral width of 0.2 nm) emerge from the spontaneous emission spectrum at the 0-1 vibronic band of p-6P. The number of these spectral lines increases with increasing of pump fluence. This lasing behavior is very similar to that reported in the previous section for films of close-packed p-6P nanofibers. As in that case, it can be attributed to coherent random lasing. The large p-6P gain bandwidth makes random lasing possible also at the 0-2 vibronic peak (visible in Figure 5.15 b) with only slightly higher threshold pump fluences.

It is evident from the spectrally-resolved emission (Figure 5.15) that spontaneous emission intensity sharply saturates for pump fluences larger than threshold fluence, in agreement with basic laser theory for a single emitter such as a single nanofiber [79]. By contrast, we did not observe this clamping of the total luminescence intensity in ensemble-average experiments, in which we collect the emission of many excited nanofibers that do not reach lasing threshold, contributing to the system response only with spontaneous emission.

Correlation between the lasing properties and the morphological characteristic of isolated p-6P nanofibers allows us to gain insight into the origin of coherent optical feedback leading to random lasing in individual nanofibers. Figure 5.16 (a) and (b) display the lasing micrograph of the selected isolated nanofiber and the emission intensity profile along the fiber, respectively. The fiber is ~100 µm long and its scattered emission appears highly spotted.

Fig. 5.16. (a): Blue levels scale image of lasing emission intensity of an isolated p-6P nanofiber. (b): Spatial profile of lasing emission intensity of the nanofiber shown in panel (a).
In order to understand the nature of the scattering centers evident in the emission micrograph, the morphology of the same fiber shown in Figure 5.16 has been studied. Figure 5.17 (a) reports the gray-scale image of the topography of the selected nanofiber, taken with the atomic force microscope in tapping mode in air. The fiber mean height and width are \( \approx 100 \text{ nm} \) and \( \approx 700 \text{ nm} \), respectively, and it is segmented by the occurrence of several breaks. The distances between consecutive cracks vary from 5 \( \mu \text{m} \) to 10 \( \mu \text{m} \) and they are 50 to 300 nm wide. It can be notice that the right side of the nanofiber (from \( X \approx 75 \mu \text{m} \) to \( X \approx 100 \mu \text{m} \)) appears divided in two nearly parallel interconnected segments, forming a double-fiber support for optical waveguiding.

By zooming in on a smaller fiber region (Figure 5.17 b) and comparing with the corresponding emission profile (Figure 5.17 c), it turns out that the scattering of the lasing emission waveguided in the nanofibers occurs at the fiber breaks. In fact, excellent correspondence is found between the position of the lasing spots and that of the fiber breaks, as shown in Figure 5.17 (b) and (c).

![Fig. 5.17. (a): Gray-scale AFM topographic image of the isolated nanofibers shown in the lasing micrograph in Figure 5.16. Black and white levels correspond to fiber height of 0 nm and 95 nm, respectively. (b): AFM zoomed image of the nanofiber region marked by the white elliptical marker in panel (a). (c): Lasing emission intensity profile of the zoomed region of the fiber.](image)

From the correlated spatially-resolved emission measurements and AFM measurements on the same \( p \)-6P nanofiber we can conclude that the fiber breaks, that occur naturally during the
growth process, introduce optical losses and partial back reflections of the waveguided lasing modes at the interfaces (where strong scattering occurs) and therefore, they are the main source of coherent optical feedback along the fiber axis responsible for one-dimensional random lasing in isolated nanofibers [80].

Measurements made on other long isolated nanofibers (> 50-100 µm) show similar results. Most individual fibers of the samples that we have studied are segmented into many homogenous sections by breaks. Figure 5.18 shows, as an example, another lasing nanofiber. As in the previous one, in these nanofibers the spatial distribution of the emission intensity, scattered to out-of-plane directions towards collecting optics, is highly inhomogeneous (Figure 18 a). Enhancement of emission scattering can be observed at the fiber break locations already below oscillation threshold, although the bright spot contrast increases dramatically above lasing threshold due to the coherent nature and directionality of the emitted light (Figure 5.18 b). The emission spectra as a function of the excitation fluence Φ (Figure 5.18 c) exhibit the typical features of the coherent random lasing, even though at a threshold excitation fluence (≈ 50 µJ/cm²) larger than that measured in the fiber previously shown.

Fig. 5.18. Optical emission intensity micrographs of lasing luminescent p-6P nanofibers excited at pump fluence of 33 µJ/cm² (a) and Φ = 170 µJ/cm² per pulse (b). (c): Time integrated emission spectra of the nanofiber placed at the centre of the X position range in panels (a) and (b), for different values of excitation fluence. The spectra are spatially integrated over the nanofiber region (from X ≈10µm to Y ≈185µm).
Experimentally, both the spectral and spatial pattern of the random modes are found to be highly reproducible over long time periods, so that we infer that the nanofibers’ material and morphology are robust against persistent laser irradiation at the pump levels used for the measurements.

5.3.2 Theoretical model for 1-D random lasing

The experimental results shown in the previous section are further supported by computer simulations of random optical spectra in one-dimensional nanostructures like our nanofibers.

We used a theoretical model that relates to the propagation of a coherent optical field of variable wavelength through a nanofiber using the transfer-matrix approach described in Appendix A. Coherent propagation (with arbitrary material gain) accounts for transmission resonances which are the relevant channels for lasing [81]. Thus, a coherent propagation model highlights all the spectral features of lasing. Calculations are done for a one-dimensional structure, neglecting cross-sectional (modal) effects. In the model structure, several material slabs, simulating fiber segments, are separated by thin air gaps, which in turn stand for fiber breaks (Figure 5.19).

Fig. 5.19. Nanofiber model used for numerical calculation with transfer matrix approach. \( d_f \) is the fiber segment length while \( d_a \) the air gap (in the selected nanofiber is: \( \langle d_f \rangle \approx 7 \mu m \) and \( \langle d_a \rangle \approx 100 nm \)).

The refractive index step between the material (\( n \approx 1.7 \) for p-6P [56]) and air causes partial back reflection of the (plane-wave) optical field at each material-air interface. The interface transfer matrix for the TM propagating mode is shown in Appendix A (A.10). Light scattering into directions other than the fiber axis at the break locations is introduced in the model in the form of linear extinction of the one-dimensionally propagating field through the air gaps. Therefore the propagation transfer matrix (A.8) is given by:
where $g$ represents the optical loss or the material gain for the transfer matrix relative to the propagation in the air gaps or in the fiber segments, respectively. Other optical losses such as material reabsorption and waveguide scattering are compensated by gain. The total loss actually determines the spectral width of the coherent propagation modes. Simulations are carried out with the structural data (deduced from the AFM) of the nanofiber shown in Figures 5.15-17, in terms of both material slab lengths and air gap widths. The intensity spectrum of the coherent field is calculated at specific break locations (break 1, 2, 3 of Figure 5.17) and compared to the lasing emission spectrum measured at the same locations (Figure 5.20).

![Figure 5.20](image)

Fig. 5.20. (a): Lasing emission spectra measured at the locations of the three nanofiber breaks shown in Figure 5.17. The pump fluence is 25 µJ/cm² per pulse. (b): Optical intensity spectra calculated at the same fiber locations on the basis of a one-dimensional coherent propagation model using transfer-matrix formalism.

The theoretical spectra are in qualitative agreement with the experimental ones, from which we infer that the present model is able to describe the basics of lasing in a 1-D random system. In particular, the model reproduces the spectral density of the lasing lines and accounts for intensity variation of the peaks as a function of the position along the nanofiber. However,
inclusion in the model of cross-sectional effects related to the propagation of light in the actual nanofiber is necessary to predict the position of the lines and their relative intensities.

The intensity spectrum is very sensitive to the shape of the nanofiber and to the structural parameter (breaks length and distribution). The photonic sensitivity of an individual nanofiber can be estimated by introducing a small structural perturbation an looking at the emission spectrum variation at some location in the nanofiber. For instance, one can neutralize the interference effects taking place at a given nanofiber break by filling its air gap with a material of the same refractive index as p-6P. Figure 5.21 shows the intensity spectrum of the random lasing emission calculated at a specific break location (solid black line), and the spectrum calculated at the same point (red dotted line), when the nearest break, which is placed at a distance of a few micrometers, is optically neutralized.

![Fig. 5.21. Optical intensity spectra at a break location (black solid line) calculated using the model based on the transfer matrix formalism. The dotted red line displays the spectrum calculated at the same fiber break after optical neutralization of the nearest break.](image)

It can be seen that variation in intensity larger than 100% occurs depending on the spectral mode. As a matter of fact, small structural perturbations (induced, e.g., by physical or chemical contaminations) can lead to huge changes in the nanofiber photonic response, thus demonstrating that p-6P organic nanofibers have potential for active photonic sensing applications.
5.3.3. Optical gain in homogeneous nanofibers

In the previous sections, we showed the experimental results of spectrally- and spatially-resolved measurements in interconnected and isolated $p$-6P nanofibers. We saw that the efficient recurrent scattering in the needle axis, caused by the fiber inhomogeneities, realizes close-loop paths for light amplification so that oscillation of random-lasing modes starts at very low excitation fluences. We showed also experimental evidence of spectral narrowing due ASE at higher pump fluences (Figures 5.6 and 5.8). However, random lasing phenomenology makes it difficult to retrieve information on the gain properties related more closely to the intrinsic photonic response of the $p$-6P nanofibers.

In the samples we studied it is possible to find shorter homogenous nanofibers in which the coherent oscillation is inhibited by removing the source of optical feedback. Therefore, these break-free fibers are suitable to single out the waveguided ASE process and to measure some fundamentals properties like the net modal gain coefficient and the stimulated emission cross-section. Breakless fibers are individuated by checking for the absence of intense scattering spots in the optical emission patterns. Figure 5.22 displays the spatially-resolved emission intensity of such a nanofiber obtained with the luminescence set-up in image configuration.

![Fig. 5.22. Time integrated optical emission micrographs of an isolated $p$-6P nanofiber excited by ultrafast pulses, for a pump fluence of 75 µJ/cm$^2$ (a) and 370 µJ/cm$^2$ per pulse (b).](image)

Figure 5.22 (a), shows the emission micrograph at low excitation fluence ($\Phi = 75$ µJ/cm$^2$). The fiber is $\approx 40$ µm long and the scattered spontaneous emission appears rather homogenous. When the pump fluence is increased above a threshold value, strong increase in the scattered...
intensity is detected at the fiber end regions (Figure 5.22.b). This behavior suggests that the waveguided spontaneous emission is amplified along the nanofiber and outcoupled at the fiber tips. The spectrally resolved intensity measurements as a function of the excitation fluence, shown in Figure 5.23, confirm this analysis.

![Figure 5.23](image)

Fig. 5.23. Time-integrated emission spectra of the nanofiber shown in Figure 5.22 for different values of the excitation fluence. The spectra are spatially integrated over the fiber region (from $Y \approx 88$ nm to $Y \approx 128$ nm of Figure 5.22).

The emission spectra are quite different from those of the inhomogeneous longer nanofibers shown in the previous sections. There is actually no evidence of lasing emission. Only weak interference fringes spaced by $\sim 0.4$ nm are revealed on the 0-1 band. However, as expected in the case of ASE, the emission spectra exhibit line narrowing for increasing pump fluence. Spectral narrowing is revealed at both the 0-1 and the 0-2 vibronic bands of $p$-6P. At excitation fluence higher than about 350 $\mu$J/cm$^2$, gain saturation effect on the 0-1 band is also evident.

Figure 5.24 displays the spatially resolved (along Y direction) spectra taken in different Y position of the nanofiber shown in Figure 5.22, for excitation fluence $\Phi = 370$ $\mu$J/cm$^2$ per pulse. The spectra are spatially integrated over a fiber region of 4 $\mu$m around the Y point indicated in the Figure. These positions can be individuated in the micrograph shown in the inset of the Figure.
Light amplification in organic self-assembled nanoaggregates

Fig. 5.24. Spatially resolved emission spectra, taken at different Y positions of the nanofiber shown in Fig. 5.22, for a pump fluence $\Phi = 370 \mu\text{J/cm}^2$ per pulse. The spectra are spatially integrated over a fiber region of 4 $\mu$m around the Y point indicated in the legend. Inset: Emission micrograph of the nanofiber at the same pump fluence.

The emission spectrum is spatially dependent: the spectral narrowing due to ASE increases going from the centre of the nanofiber ($Y = 112 \mu$m) to the tip ($Y = 91 \mu$m), because of the increase in the amplification of the waveguided light. This effect is particularly evident for the 0-2 emission band. In this spectral region actually, it can be seen gain only on the end tips of the fiber.

The lack of sharp spectral features implies the absence of coherent feedback in the fiber structure, from which we infer that the fiber tips are not characterized by very well defined facets. In order to retrieve the optical gain, breakless fibers can thus be modeled as optical amplifiers without feedback.

Fig. 5.25 (a) shows the scattered emission intensity profiles extracted from the micrographs reported in Figures 5.22 (a) and (b). While the emission profile is almost constant across the whole nanofiber at low pump fluences, above the onset of spectral narrowing the scattered intensity is position dependent and increases as the position approaches the end tips. This is consistent with the ASE process as inferred from spectral narrowing. From the emission spectrograms, we then generate two independent emission spatial profiles for the 0-1 and 0-2 emission bands, shown in Fig. 4.25 (b).
Chapter 5: Random lasing and optical gain in p-6P nanofibers

Fig. 5.25. Panel (a): Time and spatially integrated spatial profiles of the emission intensity of the nanofiber shown in Fig. 5.22, for two pump fluences: \( \Phi_1 = 75 \text{ \( \mu \)J/cm}^2 \text{ per pulse} \) (black line) and \( \Phi_2 = 370 \text{ \( \mu \)J/cm}^2 \text{ per pulse} \) (blue line). Panel (b): Intensity profiles spectrally resolved for the 0-1 (black line) and 0-2 (blue line) vibronic bands, for a pump fluence of 750 \( \text{\( \mu \)J/cm}^2 \text{ per pulse} \). The red dashed lines in both panels are fits to the data using the formula explained in the text. The fit curves are extended outside the nanofiber region for better visibility.

To estimate the amount of net gain in our nanofiber-based waveguide, we consider that ASE process, in one dimensional approximation, yields an output intensity given by [82-84]:

\[
I(L, \lambda) = A(\lambda) I_p e^{g_{net}(\lambda)L} - 1
\]

where \( A(\lambda) \) is a constant related to the cross section for spontaneous emission, \( I_p \) is the pump intensity, \( L \) is the length of the amplifying region and \( g_{net} \) the net (modal) gain coefficient defined as:

\[
g_{net} = \Gamma g - \alpha
\]

where \( g = \sigma_{SE} N \) is the material gain coefficient, \( \Gamma \) is the confinement factor of the optical intensity inside the nanofiber, and \( \alpha \) is the total propagation loss, considering material self-absorption and scattering by nanofibers surface roughness.
Inside the nanofiber of length $L$, the total intensity of the amplified light at a distance $d$ (Figure 5.26) from a fiber tip will thus be:

$$I_T(d) = I(d) + I(L-d) \propto \frac{e^{g_{net}d} + e^{g_{net}(L-d)} - 2}{g_{net}}$$

Fig. 5.26. Nanofiber micrograph with indicated the length $L$ and the distance $d$ between a generic point in the fiber and one tip.

Being the intensity profiles taken at pump fluence below the ASE onset uniform (Figure 5.25 a), we can assume that the scattering efficiency is independent of position over the whole nanofiber length. Therefore the function $I_T(d)$ can be used for curve fitting to the measured intensity spatial profiles, using $g$ as a free parameter [85]. Fit curves for $L = 40 \mu m$ are shown as the dashed red lines in Figures 5.25 (a) and (b), where the fiber tip regions are excluded from the fitting since the scattering efficiency is strongly enhanced there. For the profiles relating to the 0-1 and 0-2 bands at the highest pump fluence of 750 $\mu J/cm^2$ per pulse, best fitting yields the net gain values:

$$g_{0,1} = (1250 \pm 100) \text{ cm}^{-1}$$  
$$g_{0,2} = (750 \pm 100) \text{ cm}^{-1}$$

ASE kicks in when the net gain value is comparable to the inverse fiber length (i.e $g_{net} \cdot L = [g(\nu) - \alpha(\nu)] \cdot L \geq 1$). That is the reason why the ASE threshold fluence in short fibers is larger than that of random lasing in long fibers exhibiting several breaks.

Using the measured value of the net gain an estimate of the stimulated emission cross-section ($\sigma_{SE}$) can be made. In the limit of linear absorption of the pump energy, the excitation density ($N$) created by each pulse, at the highest pump fluence, is estimated to be $\sim 10^{20}$ cm$^{-3}$. Further neglecting population/gain time relaxation, the stimulated emission cross-section ($\sigma_{SE}$) of p-6P can be calculated from the relation [86, 87]:

$$g_{net} = \Gamma g - \alpha = \Gamma \sigma_{SE} N - \alpha$$
The optical confinement factor in typical p-6P nanofibers deposited on mica is estimated to be ~1%, while previous optical waveguiding experiments in singly selected organic nanofibers yielded \(\alpha \sim 100\text{–}300\ \text{cm}^{-1}\) (see § 3.5.2 for more details).

Using \(g_{\text{net}} = 1200\ \text{cm}^{-1}\), \(\Gamma = 0.01\), \(N = 10^{20}\ \text{cm}^{-3}\) and \(\alpha = 300\ \text{cm}^{-1}\), we obtain:

\[
\sigma_{\text{SE}} \approx 1.5 \times 10^{-15}\ \text{cm}^2.
\]

Our estimate is supported by recent experimental reports of \(\sigma_{\text{SE}}\) values as large as \(10^{-15}\ \text{cm}^2\) in films of \(\pi\)-conjugated polymers [88] and \(6 \times 10^{-16}\ \text{cm}^2\) in polycrystalline films of thiophene derivatives [89].


**6.1 Summary of results**

In this thesis, random lasing and gain properties of self-assembled organic nanofibers based on highly crystalline p-6P epitaxially grown on muscovite mica surface have been studied.

The high polarization ratio of the emission and the high bimolecular recombination rate found in these samples demonstrate the high crystal order of the nanofibers and the preferential alignment of the needles on the mica surface.

In samples with close packed nanofibers coherent random lasing emission occurs at excitation density as low as 0.5 \( \mu \text{J/cm}^2 \), in correspondence of the 0-1 and 0-2 bands of the p-6P emission spectrum. The lines spectral distribution and the threshold pump fluence of the random lasing emission depend strongly on the sample excitation region.

Correlated spatially resolved photoluminescence measurements and atomic force morphological studies on isolated nanofibers have shown the one dimensional character of random lasing in p-6P nanofibers. Coherent optical feedback is provided by multiple light backscattering at submicron-thick fiber breaks, generated during the growth process, which
interconnect contiguous fiber segments. Lasing starts when gain balances losses for the resonant modes.

A theoretical model based on a one-dimensional transfer matrix method for light propagation along the fiber has been used to describe spectral resonances observed in random lasing in nanofibers. This model allows one to reproduce the spectral density of the lasing lines and accounts for intensity variation of the peaks as a function of the position along the nanofiber and of the structural parameters of the nanofibers.

In addition to coherent random lasing, at higher excitation fluence, evidence of spectral narrowing due to amplified spontaneous emission (or, possibly incoherent random lasing) has been shown on samples with close-packed nanofibers.

In selected needles without breaks, the weaker light scattering leads to predominant amplified spontaneous emission. Amplification of waveguided light in break-free nanofibers has made it possible to estimate the net optical gain of a typical nanostructure as well as the stimulated emission cross-section, \( \approx 1.5 \times 10^{-15} \text{ cm}^2 \), which is close to the best values reported for organic materials used for laser application.

### 6.2 Potential applications of self-assembled organic nanofibers

Practical application of self-assembled organic nanofibers in photonics, optoelectronics, and related fields stems from a number of technological achievements, among which are (i) the ability of controlling the material aggregation process into highly crystalline nanofibers with suitable morphological characteristics, so as to achieve the desired photonic response (i.e., well-controlled lasing modes), and (ii) the possibility of transferring large number of homogeneous nanofibers onto substrates suitable for device realization (such as ITO, Si, and SiO\(_2\)), while ensuring a high degree of needle orientation. Concerning the transfer capability, encouraging results have already been obtained with self-assembled organic nanofibers from \( p\)-6P \cite{90} and thiophene/\( p\)-phenylene co-oligomers \cite{23}. Additional requirements depend on the specific application. In the following, we briefly discuss potential applications of organic nanofibers in photonic sensing and electrically-driven lasing.

#### 6.2.1. Prospect for electrically pumped \( p\)-6P lasing

In this section an estimate for the electrical current density which has to flow through the nanofibers film to achieve lasing threshold in continuous-wave (cw) operation are presented \cite{91}. The current density, at a given exciton population density, is derived by imposing that the total formation rate of singlet excitons is equal to the total recombination rate. The estimate is
made for the sample shown in Figure 5.1, where the lowest threshold densities have been found, and using for the singlet-singlet annihilation rate the value estimated in § 5.2. \( k_{\text{ss}} \approx 10^{-7} \text{cm}^3\text{s}^{-1} \).

For the recombination rate, density-dependent losses other than singlet-singlet annihilation are neglected. This approximation puts a lower limit to the threshold current density required for cw lasing. Within these approximations, the density of the singlet excitons is determined by the rate equation [75]:

\[
\frac{dN}{dt} = -k_0 N - k_{\text{ss}} N^2 + \frac{\xi}{\xi + 1} \frac{J}{e} = 0
\]

where \( k_0 \) is the radiative recombination rate, \( J \) the current density, \( e \) the electron charge, and \( \xi=1/3 \) is the singlet-to-triplet generation ratio [92]. The thickness of the recombination region \( d \) is set equal to the average thickness of the nanofibers (~110 nm).

The variation in singlet population density with current density \( J \) is shown in Figure 6.1. The minimum measured threshold density \( N_{\text{th}} = 6 \times 10^{16} \text{cm}^{-3} \) yields an equivalent threshold current density of \( J_{\text{th}} = 3 \text{kA/cm}^2 \).

![Fig. 6.1. Steady state singlet density versus current density, calculated using \( k_{\text{ss}} = 10^{-7} \text{cm}^3\text{s}^{-1} \). The horizontal and vertical dashed red lines indicate the threshold density and the corresponding current density \( J_{\text{th}} \).](image)

Therefore to operate at a current density \( J < 1 \text{kA/cm}^2 \), which should be sustainable in high-mobility organic crystals [75], lasing should start at a density \( N_{\text{th}} < 3 \times 10^{16} \text{cm}^{-3} \). This limit is close to the minimum threshold density reported in our samples. Furthermore, this threshold value is only a factor of three higher than the exciton density at which singlet-single annihilation process dominates the singlet recombination dynamics: \( N = k_{\text{PL}} / k_{\text{SS}} = 2 \times 10^{16} \text{cm}^3 \).

However, the question whether such current densities are sustainable in organic nanofibers based on highly crystalline materials such as \( p-6P \) calls for further experimental investigations. In fact, deep knowledge about, e.g., the electrode-induced optical losses, the breakdown electric...
field, the thermal dissipation efficiency, and the effects of ambient conditions on material
degradation, is necessary to assess the feasibility of electrically-pumped nanofiber-based
devices in a quantitative way.

6.2.2. Nanofiber-based photonic sensing

Optical interrogation of miniaturized devices based on suitable random media is currently
being envisioned as an effective solution for enabling new encoded marking and remote
monitoring capabilities for next-generation information technologies [93,94].

To this regard, we showed in § 5.3.2 that random lasing emission is very sensitive to
variation in structural characteristics of the nanofibers, e.g., position, distance, and width of the
break-induced air gaps. Simple model calculations allow us to prove the concept that small local
perturbations (induced, e.g., by chemical contamination) can lead to huge changes in the
coherent optical spectrum of a nanofiber.

We add that surface adsorption of molecular species in nanofibers assembled from suitably
functionalized oligomers [78] could generate photonic chemosensing, e.g., by modulation of the
effective index of the nanofiber propagation modes. Operation at the onset of random lasing
should lead to increased sensitivity of nanofiber-based sensors [95].

Thus, we suggest that there is potential for self-assembled organic nanofibers for photonic
sensing applications, e.g., for position sensors.

6.2 Interplay among intermolecular excitonic coupling, exciton-phonon
and exciton-photon interactions in H-aggregates: an unresolved issue.

In the second chapter of this thesis, we have reviewed the unusual emission properties of H-
aggregates in terms of a model Hamiltonian developed by Spano for pinwheel aggregates. This
was done with the aim of providing a sound theoretical framework to identify the predominant
emission transitions close to the optical gap. Spano's theoretical effort stems from the idea to
include the three basic excited-state interactions in molecular aggregates: exciton intermolecular
coupling, exciton-phonon and exciton-photon interactions. The emerging physical picture is
well described by Figure 2.7, from which we try to single out here the following three main
messages:

1) The 0-0 excitonic transition is weak or dipole-forbidden; whatever is the mechanism
   providing a finite transition dipole, the emission becomes superradiant. This latter concept
   means that the 0-0 radiative rate scales as the coherence volume of the exciton. This general
   rule should hold: the stronger the excitonic coupling, the larger the excitonic volume.
2) The 0-p vibronic replicas are dipole allowed, and polarized along the c crystal axis.
3) The overall intensity of the vibronic replicas results from the competition between intermolecular excitonic coupling and exciton-phonon interaction. When the strength of the latter interaction predominates, the intensity of vibron emissions as well as their emission cross section approach the ones characteristic of the isolated molecule. In the opposite, strong excitonic coupling regime, the generalized Franck-Condon factor is close to one, and consequently, phonon emission becomes much weaker; the overall light emission quantum yield should be also much smaller than that observed in single oligomer.

In p-6P, we have found an extraordinary large emission cross section at the 0-1 phonon emission peak, coherently with the observed high emission quantum yield (~ 30 % [47]). These data suggests that p-6P is in the weak excitonic coupling regime. Referring to Figure 2.7, we could estimate an adimensional excitonic coupling parameter $f \sim 10^{-1}$-$10^{-2}$, whereas Spano's calculations in pinwheel aggregates rather indicate $f \sim 1$, with a quantum yield around 1% [36]. This large discrepancy in the prediction of the actual radiative decay rate of H-aggregates, which in other words also means the impossibility to assess whether the excitonic coupling is in the strong or weak coupling regime, is indeed arduous to explain and deserves further theoretical and experimental investigations.

One could claim that disorder tends to localize the excitonic wavefunction, which could also be at the origin of the detection of the 0-0 spontaneous emission, otherwise symmetry forbidden in p-6P. However, this consideration appears in contrast with experimental data in other oligomer crystals. Specifically, the measured quantum yield of high quality single crystals of sexithiophene, with negligible structural disorder [96] and no violation of the emission selection rules [97], is comparable to that of the non-interacting molecule.

More insight on this basic physical issue could be provided by the experimental measure of the excitonic wavefunction delocalisation, namely, the coherent volume of the exciton [98].
Transfer Matrix Method

Consider a planar structure made of different layers of given finite thickness, infinite x-y extension, and parallel to the z axis (Figure A.1). Suppose each layer made of homogeneous materials with uniform, frequency dependent dielectric constant, which differ from layer to layer. The whole structure is thus planar and translational invariant along the plane. The propagation of a monochromatic electric field at frequency $\omega$, in absence of charge or current density, is described by the Helmholtz wave equations [70]:

$$\nabla^2 \mathbf{E}(\mathbf{r}, z) + \frac{\omega^2}{c^2} \varepsilon(z) \mathbf{E}(\mathbf{r}, z) = 0 \quad (A.1)$$

where $\mathbf{r}$ is the in plane position vector.

Fig. A.1. Example of multilayered dielectric structure with the corresponding dielectric constant profile $\varepsilon(z)$.

Because of the in-plane translational invariance, the solutions of the equation (A.1) are plane waves along the in-plane direction. For each given in-plane wave vector $\mathbf{k}_x$ and polarization we can write:
where \( \epsilon^r \) is the polarization vector. Replacing into equation (A.1) we get a one dimensional problem for the mode function \( U_{k,\omega,\alpha} \):

\[
\frac{d^2 U_{k,\omega,\alpha}(z)}{dz^2} + \left( \frac{\omega^2}{c^2} \epsilon - k^2 \right) U_{k,\omega,\alpha}(z) = 0
\] (A.3)

This equation may be separately solved in each homogeneous layer. The solution for a layer with dielectric constant \( \epsilon \) is:

\[
U_{k,\omega,\alpha}(z) = E_l \left( k_{||} \right) e^{-i k_{||} z} + E_r \left( k_{||} \right) e^{i k_{||} z}
\] (A.4)

with \( k_{||} = \sqrt{\frac{\omega^2}{c^2} \epsilon - k^2} \). \( E_l \) and \( E_r \) are complex coefficients which have to be determined by imposing the proper boundary conditions at the interface between two layers. This task can be made easily within the transfer matrix approach.

![Fig. A.2. Field propagating across the interface between two layers (1) and (2) of a planar structure.](image)

We can define for each position \( z \) in space a two dimensional vector, with components given by the two coefficients in (A.4):

\[
\begin{bmatrix}
E_r \\
E_l
\end{bmatrix}
\] (A.5)

We drop the \( k_{||} \)-dependence of \( E_l \) and \( E_r \) since the problem is separate in \( k_{||} \)-space. For an arbitrary structure, like that shown in Figure A.2, we can write the field in the form (A.2) for each \( z \) position of the two given layers (1) and (2). The boundary conditions at the interface
between the layers will result in a linear relation between the coefficients of the field in the two regions, which can be written as:

\[
\begin{bmatrix}
E_r^{(2)} \\
E_i^{(2)}
\end{bmatrix} = \begin{bmatrix}
M_{11}^{(21)} & M_{12}^{(21)} \\
M_{21}^{(21)} & M_{22}^{(21)}
\end{bmatrix} \begin{bmatrix}
E_r^{(1)} \\
E_i^{(1)}
\end{bmatrix}
\]

(A.6)

The matrix \(M^{(21)}\) thus defined is the interface transfer matrix of the structure we are considering.

The most important property of transfer matrix is that they can be composed to obtain transfer matrix of complex structures. This means that, given for example the structure shown in Figure A.3, characterized by transfer matrixes \(M^{(21)}\) and \(M^{(32)}\), the transfer matrix of the overall structure is simply \(M^{(31)} = M^{(21)} M^{(32)}\), and the coefficient of the field in a \(z\) position of the region (3) are related to those in the layer (1) by the relation:

\[
\begin{bmatrix}
E_r^{(3)} \\
E_i^{(3)}
\end{bmatrix} = M^{(31)} \begin{bmatrix}
E_r^{(1)} \\
E_i^{(1)}
\end{bmatrix}
\]

(A.7)

Hence, starting from the matrices for the simplest element, namely the homogeneous layer of a given thickness and the simplest interface, one can derive the wave propagation for arbitrarily complex layered structures.

---

![Fig. A.3. Field propagating on a multilayered structure.](image)

It can be shown that the transfer matrix corresponding to the propagation from \(z_1\) to \(z_2\) in homogeneous medium (Figure A.3) is given by [99]:

\[
M_{\text{hom}} = \begin{bmatrix}
e^{ik_1(z_2-z_1)} & 0 \\
0 & e^{-ik_1(z_2-z_1)}
\end{bmatrix}
\]

(A.8)

The transfer matrix for an interface between two dielectric layers with refraction index \(n_1\) and \(n_2\), is different for the two different polarizations TE (Transverse Electric) and TM (Transverse Magnetic) of the electromagnetic field. Applying the Maxwell boundary condition, it can be shown that the interface transfer matrix for the TE polarization is given by:
\[ M_{TE} = \begin{bmatrix} \frac{k_z^{(2)} + k_z^{(1)}}{2k_z^{(2)}} & \frac{k_z^{(2)} - k_z^{(1)}}{2k_z^{(2)}} \\ \frac{k_z^{(2)} - k_z^{(1)}}{2k_z^{(2)}} & \frac{k_z^{(2)} + k_z^{(1)}}{2k_z^{(2)}} \end{bmatrix} \quad (A.9) \]

while for the TM polarization is:

\[ M_{TM} = \begin{bmatrix} \frac{n_z^{(2)}k_z^{(1)} + n_z^{(1)}k_z^{(2)}}{2n_1n_2k_z^{(2)}} & \frac{n_z^{(2)}k_z^{(1)} - n_z^{(1)}k_z^{(2)}}{2n_1n_2k_z^{(2)}} \\ \frac{n_z^{(2)}k_z^{(1)} - n_z^{(1)}k_z^{(2)}}{2n_1n_2k_z^{(2)}} & \frac{n_z^{(2)}k_z^{(1)} + n_z^{(1)}k_z^{(2)}}{2n_1n_2k_z^{(2)}} \end{bmatrix} \quad (A.10) \]

Here \( k_z^{(j)} = \sqrt{\frac{\omega^2}{c^2} \varepsilon_j - k_{jj}^2} \), where \( j = 1, 2 \) indicate the left and right side of material, respectively, and \( n_j = \sqrt{\varepsilon_j} \).
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Publications

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